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SULFIDE OREBODIES AT YAURICOCHA, CENTRAL PERU —REPLACEMENTS OF ORGANIC REEFS?

HECTOR J. WARD

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ABSTRACT

Yauricocha is about 60 miles due south of La Oroya in Central Peru. The rocks of the area are limestones, shales and monzonite porphyry, all of which are partly covered by alluvium and glacial deposits. The limestone consists of light-gray, thin-bedded and massive rocks of Middle Cretaceous Age. Filled and partly filled cavities are abundant.

Some of the ore deposits are masses of pyrite that have replaced limestone. Ore minerals are zoned in accordance with the textural types of pyrite.

Scour and fill, bedding and laminations in the pyrite are considered to owe their origin to sedimentary processes and not to Locke's mineralization

stoping. The spatial distribution of the different types of pyrite prompts the suggestion that the replaced sedimentary structures developed in an organic reef environment rather than in limestone caves. The possible reef origin of the sedimentary structure stresses the importance of observing lithological changes in limestone to lessen the element of chance in the search for ore deposits.

INTRODUCTION

THE writer, when at Yauricocha mine in Central Peru for a short period in 1955, was intrigued with the spatial distribution of two textural types of

FIG. 1.

pyrite that form the main primary sulfide body. Later, in 1957, sketches made during routine work were assembled in an effort to explain the origin of a mass of pyrite with a core of massive, dense pyrite separated from the country rock in most places by a zone of fragments and angular boulders of massive, dense pyrite set in a matrix of friable, sandy-textured pyrite.

The structures and textures within the sulfide mass are of sedimentary origin and not the result of mineralization stoping. The writer considers the theory that the orebody is more likely to be a replacement of an organic reef than of a filling in a limestone cave.

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The writer wishes to thank Dr. G. C. Amstutz, Missouri School of Mines, Dr. F. L. Humphrey, Stanford University, V. C. McKelvey, United States Geological Survey, and Stanton B. Keith, Cerro de Pasco Corporation for helpful discussions and criticisms. The observations were collected when the writer was at Yauricocha for a short period in 1955 and reviewed at Stanford University in 1957. The encouragement and permission of the Cerro de Pasco Corporation to publish this paper is gratefully acknowledged; the ideas presented herein are the sole responsibility of the author and do not reflect the official position of the Corporation.

Location.—The Yauricocha mine (Fig. 1) is about 60 miles due south of La Oroya in Central Peru. It is on the western side of the Continental Divide at the headwaters of one of the branches of the Rio Cañete, which flows into the Pacific Ocean.

The surface workings of the mine are between 4,600 meters and 4,650 meters above sea level. They lie in a broad U-shaped basin, about 5 kilometers long, which trends northeasterly.

GENERAL GEOLOGY

The rocks of the area are limestones, cherts, shales and monzonite porphyry, all of which are partly covered by alluvium and glacial deposits.

The following stratigraphic column has been recognized for the Yauricocha area by geologists of the Cerro de Pasco Corporation.

Quarternary: Glacial deposits

Tertiary: Monzonite porphyry intrusives

Casapalca red beds:

Triada member consisting of 100 ms of interbedded cherts and limestone

Quishuarnioc limestone consisting of 40–80 ms of interbedded chert, shale and limestone

France chert, 130 ms of pyritized chert

Cretaceous: Machay limestone:

Huamanripa limestone, ? meters, massive, gray limestone with thin silty beds and basalt sill 13 ms thick

Machay Limestone.—Machay limestone is light-gray in color, and has both thin-bedded and massive beds. In the mine area, the limestone is a coarse to fine-grained recrystallized rock. The color of the limestone depends on the degree of alteration produced by the igneous intrusives.

A fine-grained, thinly-laminated, light-colored, discontinuous siltstone bed about 5 ms wide is in the limestone. The siltstone bed changes along its strike into limestone or limestone breccia. The abrupt change in some places

is due to displacement along minor faults but in others is possibly depositional.

Noble (9) reports the presence of fossils in open spirals and probable crinoids from Cerro Huamanripa about half a kilometer to the north-east of the mine. No reference (3, 8) is made to the occurrence of organic reefs in the Machey limestone.

Cavities in the Limestone.—Filled and partly filled solution cavities are abundant. The partly filled solution cavities, probably of Recent age, contain debris and travertine. One of the largest cavities in the mine is 20 ms by 10 ms by 30 ms.

The filled cavities in the limestone, which rarely attain dimensions greater than 20 cubic meters, contain sandy and argillaceous beds. The argillaceous

FIG. 2. Argillaceous rock from filled cavity near Central Shaft, 575 level.

beds in one instance are deformed (Fig. 2). The sediments in the filled cavities have variable dips. The filled cavities are thought to be older than the partly filled cavities because they are mineralized in places.

Breccias in the Limestone.—Fault and contact breccias occur in the limestone. Other breccias not associated with faults or intrusives formed as sediments, possibly adjacent to organic reefs.

Casapalca Red Beds.—The Casapalca red beds are red shales and sandstones overlying tactites and impure limestone beds known as France chert. Sigrist (11) considers that the France chert was probably formed by the contact metamorphism of the original rocks, which were possibly shales, marls and sandy limestones.

The contact of the Casapalca red beds with the Machay limestone at

Yauricocha seems to be conformable. Harrison (3) has found that west of La Oroya and south of Morococha the Casapalca red beds lie on the Machay limestone without an angular unconformity. To the north of Morococha, Harrison and McLaughlin (8) have reported a marked angular unconformity between the two formations.

Monzonite Porphyry Intrusives.—Two large masses of monzonite porphyry and several small masses crop out. The largest outcrop, 39 square kilometers in area, lies to the south of Yauricocha. The smaller of the two

FIG. 3.

masses occupies the central part of the Yauricocha basin and is about 11 square kilometers in area. The small masses of monzonite porphyry are offshoots of the stocks. The intrusives that have marblized the limestone are strongly jointed. Some joints are now occupied by veins. In places the contact of the intrusives with limestone shows some degree of brecciation.

STRUCTURE

The Yauricocha mine is on the western limb of a south-easterly plunging syncline. The dip of the beds is from 60° to 70° to the northeast.

The siltstone bed in the Machay limestone, despite its lateral and vertical discontinuity, has been found in the lower levels of the mine on the downward projection of its dip from the upper levels. This indicates that the limestone is not isoclinally folded in the vicinity of the mine workings and consequently the limestone breccias that cut across them are not isoclinally folded.

Pre-mineral and post-mineral fractures are present, but faulting on a large scale is not evident.

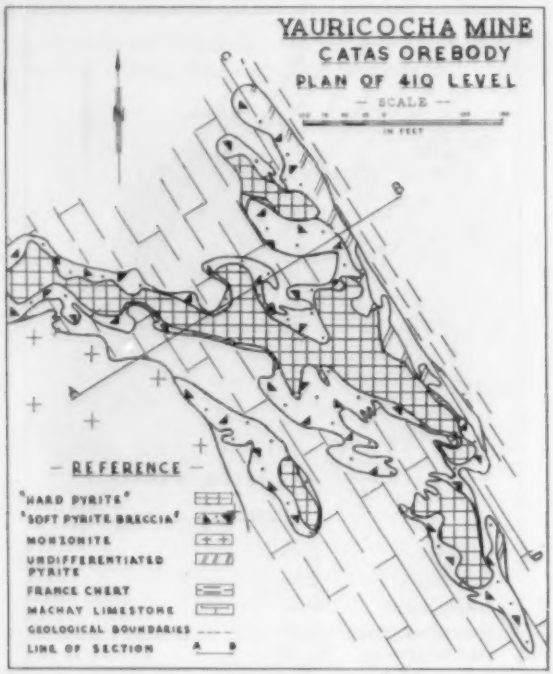


FIG. 4.

ORE DEPOSITS

The ore deposits (Fig. 3) are in massive, dolomitized, Machay limestone near its contact with the France chert. The principal sulfide orebodies are Catas, West Catas, Pozo Rico, Eastern Contact and Mascota, all of which are near the Mascota and Central Shaft monzonite stocks. The West Catas and Eastern Contact orebodies are westward extensions of the Catas orebody.

Copper and lead-zinc minerals are mined from the supergene and hypogene zones. One orebody is oxidized to 575 ms below the surface. The oxide orebodies have been described by Lacy (5) and will not be discussed here.

Hydrothermal alteration of the monzonite and country rocks, together with the presence of small copper- and lead-zinc-bearing veins in the monzonite, the Machay limestone and the Casapalca red beds, points to an epigenetic origin of the veins and orebodies.

Pyrite is the dominant sulfide mineral. It occurs as irregularly-shaped masses up to 250 ms long, 60 ms wide and extending downwards for nearly 300 ms. The core of a pyrite mass (Figs. 4, 5, 6) is massive, dense pyrite, known as "hard pyrite", separated from the country rock in most places by

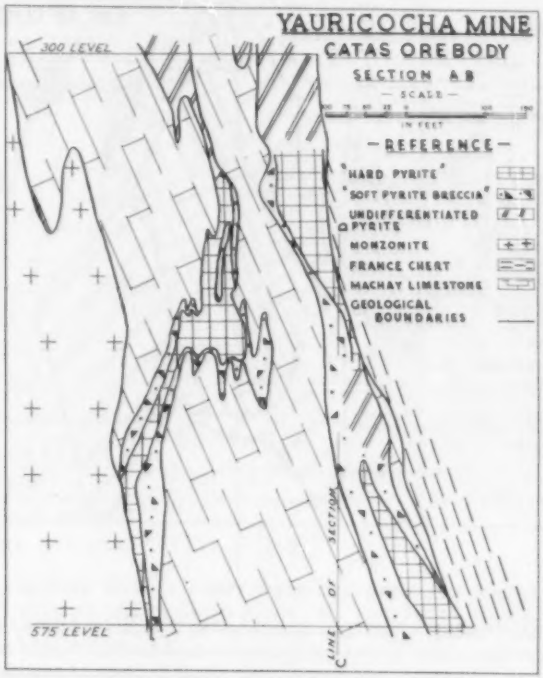


FIG. 5.

a zone of "soft pyrite breccia" which consists of fragments and angular boulders of dense pyrite ("hard pyrite") in a friable matrix of sandy-textured, fine to coarse-grained pyrite. Where fragments and boulders of "hard pyrite" are absent the friable pyrite is mapped as "soft pyrite." Areas in which detailed information regarding the type of pyrite is not available are shown as undifferentiated pyrite in the accompanying illustrations. The terms in italics will be used throughout and for the purpose of discussion the term "soft pyrite breccia" will include "soft pyrite."

Enargite, chalcopyrite and tennantite are predominantly in the core of "hard pyrite," whereas galena and sphalerite replace "soft pyrite breccia."

Mine mapping (Fig. 7) and microscopic examinations of polished sections (Amstutz) [1] have shown that the pyrite has replaced limestone and limestone breccia. In many places "soft pyrite breccia" contains fragments and boulders of enargite-bearing "hard pyrite" and altered limestone. Some boulders of "hard pyrite" have a core of silicified limestone.

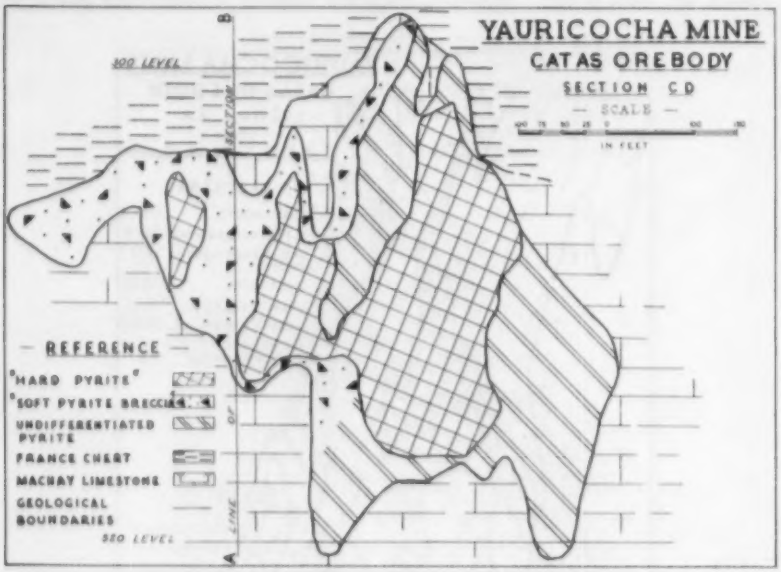


FIG. 6.

RELICT TEXTURES AND STRUCTURES IN THE OREBODIES

The relict structures observed in the Catas and West Catas orebodies and the sulfide portion of the Pozo Rico orebodies will be commented on.

Laminations, bedding and scour and fill structures, have been mapped. No fossils have been observed in or reported from the sulfide bodies, but the writer thinks that some of the structures which he saw when in the mine may represent replaced algae (Fig. 8).

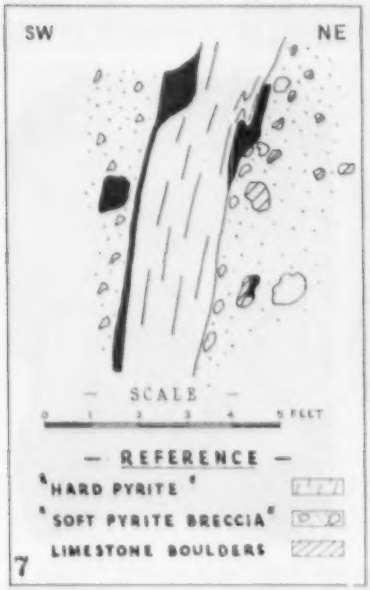
Relict structures where seen in the "hard pyrite" consist of poorly defined, discontinuous laminae and bedding. Best examples of laminae (Figs. 7, 9) and bedding (Fig. 10) are in boulders and lenses of "hard pyrite" in "soft pyrite breccia" or near the boundary of the core with the border zone.

Dark and light-colored beds in the "soft pyrite breccia" are probably the result of selective replacement of the original sediments. Light-colored beds consist principally of white clayey material containing little pyrite.

[1] Personal communication.

Scour and fill structures were mapped in a few places. In one place (Fig. 11), a transition from "soft pyrite breccia" with boulders of red chert through "soft pyrite breccia" with fragments and boulders of limestone to limestone breccia was noted. In another locality (Fig. 12) the change is from "hard pyrite" to "soft pyrite breccia."

The size of the fragments and boulders of limestone ranges from microscopic to 1.5 meters by 1.7 meters. "Hard pyrite" within "soft pyrite breccia" ranges from microscopic size to boulders 30 cm in diameter. The average



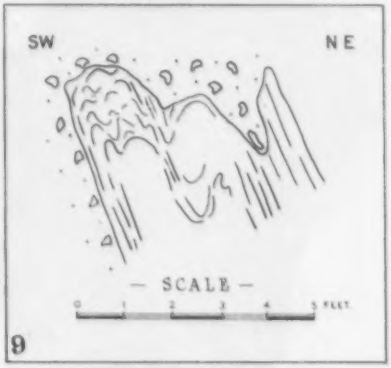


FIG. 7. Tongue of bedded "hard pyrite" in "soft pyrite breccia." Note replacement by enargite (black) of limestone and "hard pyrite" boulders. One boulder (lower right) of limestone is partly replaced by pyrite and enargite.

FIG. 9. Tongue of bedded "hard pyrite" surrounded by "soft pyrite breccia." See Figure 7 for reference to symbols.

size of the pyrite boulders is about 8 cm in diameter. It has been observed that some of the larger boulders of unreplaced limestone are near the contact of the "soft pyrite breccia" with the country rock. Abundant laminated boulders of sulfide-veined red chert probably formed by the silicification and haematization of limestone boulders occur within the pyrite mass. The contact of the pyrite and the limestone is generally sharp and irregular. The pyrite tongues into the limestone.

In several mine openings limestone boulders and fragments in a dark carbonaceous matrix grade through limestone fragments in a hydrothermally

bleached matrix to a lead-zinc bearing "soft pyrite breccia" containing partly replaced limestone boulders (Fig. 13).

INTERPRETATION OF STRUCTURES AND TEXTURES IN TERMS OF ENVIRONMENT OF DEPOSITION

General.—The formation of pipelike masses of sulfides in limestones has been discussed by Walker (14) and Locke (6) and commented on by McKinstry (7).

Walker divided limestone caves into two classes, namely, those formed by cold descending surface waters and those formed by hot ascending solutions

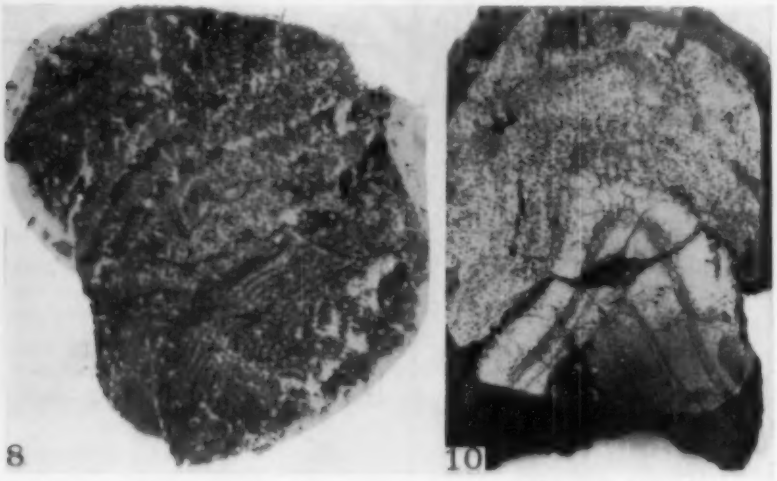


FIG. 8. Replacement of ? algal structure, 410 level, Catas orebody (× ¾).
FIG. 10. Boulder of "hard pyrite" found near contact of "hard pyrite" and "soft pyrite breccia," Catas orebody, 410 level (¾ natural size).

of deep origin of circulation. Pre-existing structures and the relative solubility of the strata traversed control the formation of caves. The caves formed by cold descending waters are irregularly oval or elliptical in cross-section with the long axis of the cave being several times greater than the short axis.

"Cave earth" and "cave breccia" are deposited in the openings. The "cave earth" contains material brought in by the descending waters in addition to the fine-textured debris formed in the cave. The environment is sedimentary and consequently bedding is developed.

Walker considered that caves formed by hot ascending solutions would contain less "cave earth" because no extraneous material is being carried by the solutions. The cross-section of the cave would be more uniform as the

ascending solutions would not be joined by tributaries as is the case when caves are being formed by descending solutions.

Locke, in his theory of "mineralization stoping," considers that the hot ascending solutions which are the forerunners of the ore stoped their way upwards along pre-existing fractures to form a pipe-like mass of breccia. The breccia so formed was later partly or wholly replaced by ore.

Reynolds (10) classified the sedimentary origin of breccias. One of the classifications was that of breccias formed by wave and current action around coral reefs.

The use of the term reef has been discussed at length by Cummings (1) and Twenhofel (12). Twenhofel understands an organic reef to be "an aggregate of organic material of significant dimensions built in part by colonial organisms, mainly but not necessarily marine. . . ." The definition of

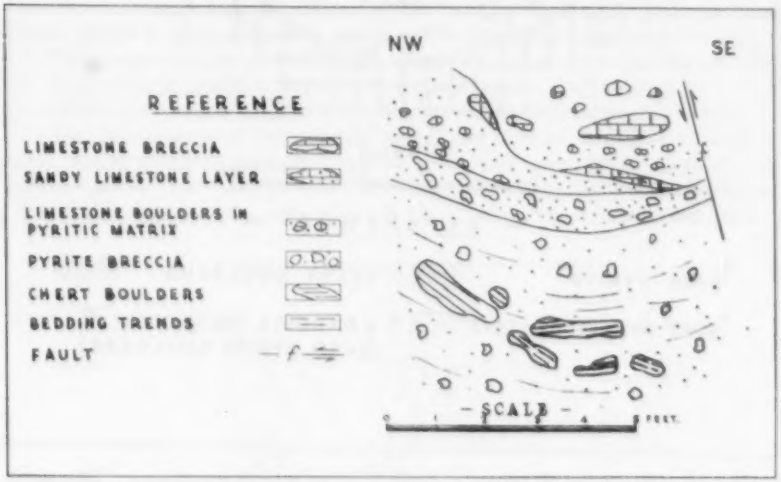


FIG. 11. Scour and fill structure in "soft pyrite breccia." The "soft pyrite breccia" with chert boulders grades upwards through limestone boulders in a pyritic matrix to limestone breccia.

Vaughan (13) is essentially pictorial. Vaughan defines a coral reef as "a ridge or mound of limestone, the upper surface of which lies, or lay at the time of formation, near the level of the sea, and is predominantly composed of calcium carbonate secreted by organisms, of which the most important are corals." However, later work has shown that lime-secreting algae are the most important contributors to the formation of reefs not only in the Present but also in previous Geologic Eras.

The ridge or mound in modern terms is the core. The nature of the reef core is variable. It may be massive with little or no bedding, a porous irregular mass of well-cemented dolomitized coquina, or a loosely consolidated

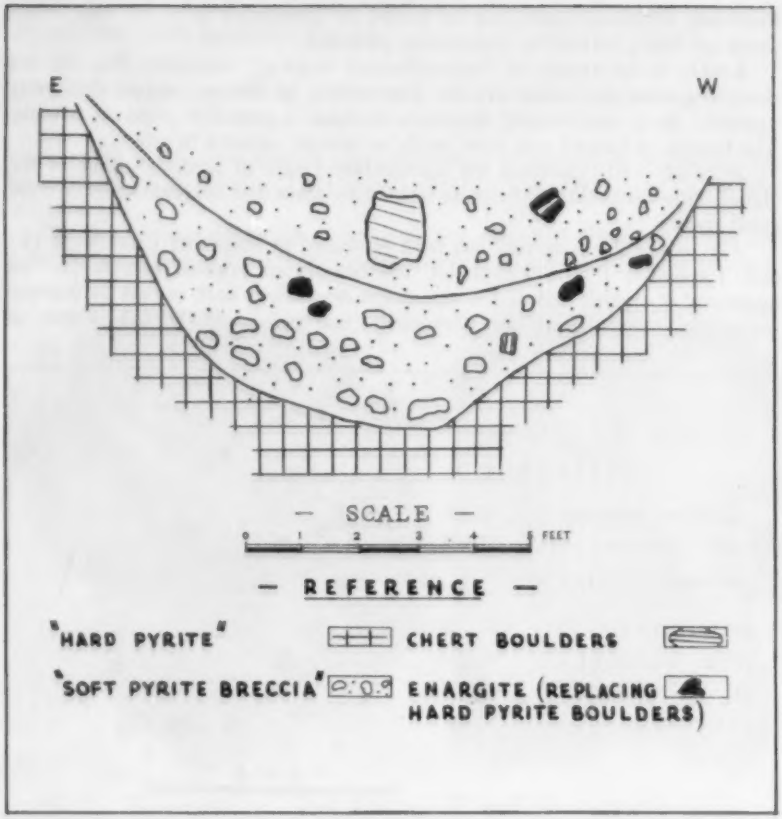


FIG. 12. Scour and fill in "hard pyrite." Note breccia size change. In mine it was observed that a narrow layer, one to two inches thick, of white clay of hydrothermal origin, separated the "soft pyrite breccia" from the "hard pyrite."

mass of breccia and rubble as implied by Walther (15). Talus derived from the reef by wave action surrounds the core of the reef. The talus is generally composed of calcareous sands, gravels and breccias, which in places have been observed to contain argillaceous material (2). The inclination of the talus around the reef is variable and depends on the type of reef. Cummings and Shrock (2) have described the steep dips of the sediments associated with the Niagaran coral reefs of Indiana. In Europe, flatly dipping beds have been observed. The reef talus may be bedded and have structures such as scour and fill and slumped bedding. The transition from the sediments of the reef complex into normal sediments may be gradual or abrupt. Reef talus will also contain fragments and boulders of adjacent sediments.

Post-depositional processes such as silicification and dolomitization may completely alter the reef complex so that only a general distinction can be made between the reef core and talus.

At Yauricocha.—In determining whether the sulfides replaced cave fillings, formed by descending solutions, mineralization stoping, or an organic reef, the critical points to be considered are the contact of the "soft pyrite breccia" with the country rock, the spatial distribution of the flanking "soft pyrite breccia" with respect to the "hard pyrite" core, and the internal structures and textures of the deposit.

The distal flanking beds of an organic reef form an abrupt or gradational contact with the sediments beyond the reef. Cave fillings, which have reasonably sharp wall contacts in most places, seem to intertongue with other sediments where the cave developed along joints or bedding planes. Thus, reef talus and cave fillings may have sharp contacts with the surrounding sediments and consequently the contact of the "soft pyrite breccia" with the limestone, which is sharp and irregular, is not, in itself, a positive criterion.

The general picture of the Catas orebody and its westward extension (Fig. 4) is a mass of pyrite with a core of "hard pyrite" surrounded by a "soft pyrite breccia" which tongues into massive altered limestone.

The replacement of "cave earth" and "cave breccia" found in a limestone cave would probably produce a sulfide mass with alternating layers of "soft pyrite breccia" and "soft pyrite." No core of "hard pyrite" would be formed in the process unless a tremendous block of limestone collapsed into such a

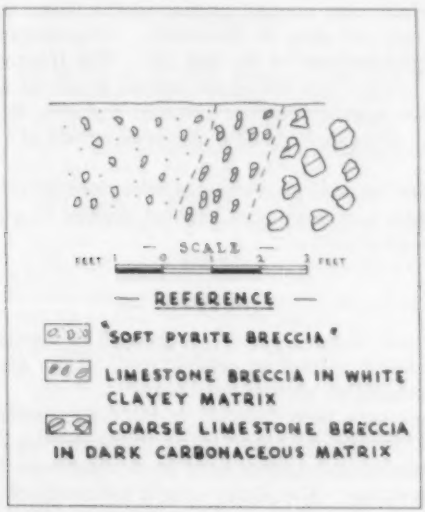

SCALE
FEET 1 0 1 2 3 FEET
REFERENCE
"SOFT PYRITE BRECCIA"
LIMESTONE BRECCIA IN WHITE CLAYEY MATRIX
COARSE LIMESTONE BRECCIA IN DARK CARBONACEOUS MATRIX

FIG. 13. Sketch from a stope on the 520 level, showing the change from limestone breccia through a limestone breccia with a hydrothermally bleached matrix to "soft pyrite breccia."

cave. Similarly, the general arrangement of the different types of pyrite would not result from the replacement of a jumbled mass of breccia likely to be produced by mineralization stoping.

Replacement of an organic reef flanked by reef talus could probably result in the formation of a core of "hard pyrite" surrounded by "soft pyrite breccia."

Bedding and scour and fill structures are common to organic reefs and cave fillings. Cave fillings have low initial dips. Reef talus may dip steeply or flatly away from the reef core.

At Yauricocha, if the sulfide bodies replaced cave fillings dips of replaced beds are probably initial dips. If the Catas orebody and its westward extension are a replacement of an organic reef the orebody should be restored to an approximately horizontal position. This can be accomplished by tilting Figure 6 seventy degrees and tilting Figures 4 and 5 until the contact of the France chert with the Machay limestone is horizontal. Figure 6 becomes a plan of the reef surface and Figures 4 and 5 become vertical sections that are very similar to sections of transgressive or regressive reefs as illustrated by Henson (4).

Bedding in the "soft pyrite breccia" not only may be vertical but may dip flatly away from the "hard pyrite." Restoration of the measured bedding attitudes to an approximate initial position showed their variability and stressed the need for closer observations as more mine openings are made for the extraction of lead-zinc ores.

Reef breccias consist of bioclastic and biolithic material. Fragments and boulders of the reef rock are embedded in poorly-cemented calcareous sand. "Cave breccia," which may contain outsize blocks, have the texture of the source rocks and may not even be limestones. Replacement processes have obscured many of the textures in the breccias. The fragments and boulders in the "soft pyrite breccia" are limestone, altered limestone and "hard pyrite" set in a soft, friable matrix which is possibly replaced, loosely-consolidated calcareous cement. This suggests more the replacement of a reef breccia than a "cave breccia."

The "hard pyrite" core in places has cavities lined by enargite, pyrite and quartz. The cavitites may have been original cavities in a reef core and not formed by hydrothermal activity.

CONCLUSIONS

The structures and textures possibly originated in a sedimentary environment such as that found around an organic reef. They are not the product of mineralization stoping as depicted by Locke.

The observations have been confined to the Catas orebody and its westward extension. However, in several places in the district limestone breccias with bedded and laminated boulders have been observed. Ore is associated with some of the breccias. The Exito mine 6 km south of Yauricocha is in limestone breccia near the Machay limestone-monzonite porphyry contact. The Antonio mine in a similar geological setting is halfway between Yauricocha and Exito.

Insufficient work has been done to establish a structural control but evidently a lithologic control between limestone breccias and monzonite porphyry intrusives exists. Should the limestone breccias represent a variety of organic reefs, as such, they are especially favorable for ore deposition.

According to Twenhofel (12), organic reefs are present in every system beginning with the Huronian. Oil geologists have found that reefs are present in most extensive formations of limestone.

Three general zones in the reef environment are porous and consequently extremely favorable locii for the entrapment of oil. The general zones are the reef itself, the flanking strata and the overlying strata. The same zones, on account of their porosity, would also be favorable to the deposition of ore minerals.

The economic importance of implications of a reef origin for the breccias cannot be sufficiently stressed. Copper orebodies may be detected by surface showings of lead-zinc minerals in some places. Small scale structural features that may be necessary for the entry of the ore-bearing fluids to the porous reef zones can be easily overlooked. Organic reefs are not regularly distributed nor are they all alike. Therefore the lithological changes in limestone must be closely observed in order to determine the trend of the preexisting shoreline and the likely distribution of organic reefs.

165 South Terrace,
Como,
Western Australia,
March 2, 1959

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THE TITANIUM MINERALOGY OF CERTAIN BAUXITES AND THEIR PARENT MATERIALS

JAMES A. HARTMAN

ABSTRACT

The titanium mineralogy of bauxites, associated clays and parent rocks from Arkansas, France, Jamaica, Oregon, Ireland and Surinam has been investigated. The most abundant titanium oxide in the parent rocks is ilmenite. Very small amounts of leucoxene, rutile, anatase and titaniferous hematite are also present. These same minerals plus titaniferous magnetite and menaccanite occur in the clays and bauxites but in different relative percentages. Leucoxene, an alteration product of ilmenite, is a major constituent of the + 325 mesh heavy mineral fractions of bauxites and associated clays. X-ray studies show that leucoxene in these materials consists of rutile and anatase. The alteration of primary ilmenite to secondary oxides follows three different routes. In general, the nature of the parent rock appears to exert little if any influence on the formation of the TiO_2 polymorphs from ilmenite or on the alteration products of ilmenite, although the modes of alteration are more varied in Arkansas bauxite than in bauxite from the other localities. The bulk of the TiO_2 in bauxites and associated clays is in the − 325 mesh fraction. This finely divided TiO_2 comes in part from the titanium released during the alteration of sphene and other titanium-bearing silicates of the parent rocks and in part from the alteration of ilmenite.

INTRODUCTION

A CHEMICAL analysis of any bauxite, regardless of the type of rock from which it is derived, invariably indicates the presence of TiO_2. Ore bodies within a district commonly show a uniform content of TiO_2, but from district to district the content of TiO_2 ranges from 2 to 9 percent. Bauxites derived from basalts generally contain higher percentages of TiO_2 than deposits derived from sedimentary rocks or syenites.

The titanium mineralogy of most bauxite deposits is imperfectly known for at least two reasons: 1) fine-grained mineral aggregates involved are difficult to identify; and 2) laborious techniques must be used to collect fine-grained aggregates for detailed study. Petrographic studies yield only partial information. The white opaque alteration products of ilmenite and other titaniferous minerals observed in thin sections of bauxite must generally be classed simply as "leucoxene," since one cannot determine petrographically whether anatase, rutile or brookite is present. Because of the above factors the titanium mineralogy of bauxites has received only cursory treatment by most geologists who study these deposits. This is unfortunate because a fuller knowledge of the titanium minerals and the conditions under which they form might aid the geologist in deciphering the process of bauxitization.

Titanium metal has properties which make it useful in many industries provided that it could be produced at a reasonable cost. The titanium metal industry is only in its infant stages. It has been beset by many problems, primarily of a metallurgical nature, which have raised the price of the metal beyond the point where it can compete with steel and other metals. When the metallurgy has been solved, however, titanium metal will undoubtedly be used along with the common metals of today. At that time additional reserves of titanium ore will have to be found. Bauxite residues represent a source of titanium ore which could be utilized at that time. It is necessary, however, to have a detailed knowledge of the mineralogy before their value as potential titanium reserves can be evaluated. The mineralogy of the + 325 mesh fraction is especially important since the coarser grained minerals are most readily recovered by ordinary processes of beneficiation.

Purpose and Scope.—The present study was undertaken to obtain information on the following points:

1. The titanium mineralogy of heavy mineral residues obtained from certain bauxite samples.
2. The alteration of primary titanium-bearing minerals to secondary titanium oxides.
3. The effect of the parent material on alteration of the primary titanium minerals.
4. The distribution of the titanium minerals in various size ranges.
5. The mineralogical composition of leucoxene in bauxitic materials.
6. The factors that control the formation of the three TiO_2 polymorphs (rutile, brookite and anatase).

Samples from six districts—Arkansas, France, Jamaica, Oregon, North Ireland and Surinam—have been examined. In these districts bauxites derived from syenite, limestone, basalt and noncalcareous sediments are represented. These are the four major rock types from which bauxite deposits of the world are derived.

Acknowledgments.—The following organizations and individuals have contributed samples from the districts bracketed: Reynolds Metals Company and Aluminum Company of America (Arkansas), especially Dr. John H. Moses and Mr. Otis Clarke, Jr., of the former company and Mr. George C. McBride of the latter organization; the State of Oregon Department of Geology and Mineral Industries (Oregon); Pechiney Compagnie de Produits Chimiques et Electrometallurgiques (Southern France); Reynolds Jamaica Mines, Ltd. (Jamaica); Dr. Wilson D. Michell (Surinam); and Dr. E. N. Cameron (North Ireland).

Mr. R. K. Sorem took the photomicrographs for the writer. This investigation was conducted in the Laboratory of Economic Geology at the University of Wisconsin under the direction of Dr. E. N. Cameron. His encouragement and advice during the course of this work were greatly appreciated. The funds for this study were supplied through the Union Carbide Research Fellowship in Economic Geology. This aid is most gratefully acknowledged.

REVIEW OF LITERATURE ON TITANIUM MINERALOGY IN VARIOUS BAUXITE DISTRICTS

The literature on the general subject of bauxites and laterites is voluminous, but certain aspects of the mineralogy of bauxitic materials are incompletely understood. The occurrence and origin of titanium is one such aspect. In Arkansas the bauxite deposits are residual accumulations derived from weathering of nepheline syenite. Mead (33) states that Arkansas bauxite contains ilmenite and titanite and possibly some pseudobrookite and perovskite. Bramlette (7) found ilmenite and titanite in the syenite. He reported that in bauxite titanite alters to "xanthitane" and that rutile is a minor constituent. Frederickson (18) states that titanite, ilmenite, brookite and small amounts of anatase occur in these deposits. Calhoun (12) reported manganilmenite and minor amounts of rutile and leucoxene.

Irish bauxite is derived from the alteration of basalts and rhyolitic debris. Eyles (16) found anatase and minor amounts of rutile and ilmenite but no brookite in these ores. Bauxite from Oregon is also a residual product of basalts. Libbey, Lowry and Mason (31) concluded that ilmenite may be present. Allen (1) reported titaniferous magnetite and minor anatase in the Oregon material. Roedder (14) found ilmenite and minor titaniferous magnetite.

Bauxite from Jamaica and France is a residual accumulation from limestone. Hartman (24) reported ilmenite, rutile, leucoxene, titaniferous magnetite and titaniferous hematite in the Jamaican ores. Lapparent (29, 30) found anatase and rutile in the French ore.

Surinam bauxite is derived from weathering of non-calcareous sediments. Ijzerman (26) reported leucoxene, and Van Kersen (42) found rutile and anatase in these ores. Brindley and Sutton (9) have recently recorded anatase from nearby British Guiana bauxite.

PREPARATION OF SAMPLES

Bauxite samples studied range from soft and friable to hard and dense. The hard and dense specimens, e.g., Arkansas and France, were coarsely crushed in a jaw crusher. Lumps in the soft ores were broken up by kneading. A sample weighing from 150 to 1,000 grams was digested in hot concentrated NaOH. After several hours of digestion the solution was decanted and washed on a 325-mesh sieve. Grains remaining on the sieve were returned to the sample, and digestion was repeated until all the alumina was removed. Particles passing through the sieve were discarded.

Because most bauxites contain finely divided earthy hematite the residues were digested in a solution of 1 : 3 HCl with stannous chloride used as a reducing agent, in order to remove iron oxide. This solution was neutralized, dispersed and mechanically agitated for about fifteen minutes. The mixture was washed on a 325-mesh sieve, and the + 325 mesh material was returned to the residue.

The clays were dispersed and washed on a 325-mesh sieve. The material retained on the screen was returned to the beaker. This process was repeated until all the clay-sized particles were removed.

Treatment of the parent material depended on the type of rock. The limestones, after coarse crushing, were digested in 1:3 HCl. Syenites and basalts were crushed to pass a 12-mesh sieve. A sample of each syenite and basalt, weighing approximately 100 grams, was separated into a float and a sink fraction in acetylene tetrabromide (S.G. 2.9). The float fraction was pulverized and resettled, and sink fractions from the two steps were mixed together.

Each residue obtained from the bauxites and clays was separated into a sink and a float fraction. The sink fraction was weighed and sieved into the following five size fractions: + 40, − 40 + 100, − 100 + 140, − 140 + 200, − 200. A split of each of these fractions was briquetted and polished. Because the parent rocks were pulverized prior to recovering the heavy minerals, a grain size analysis could not be made, but a sample of the total heavy mineral fraction of each parent rock was briquetted and polished.

RESULTS OF POLISHED SURFACE STUDY

General Statement

During the course of this examination over 115 polished surfaces were studied. The results, by district, are given in Tables 1–6. The residues were not examined in transmitted light; hence the silicates were not identified.

In Tables 1–6 the numbers given on the third line from the top, denoted "% Heavies of Sample," refer to the percentage of heavy mineral obtained from the sample on an "as received" basis. Column 1 for each sample in these tables gives the percentage of each mineral in the heavy mineral fraction. Column 2 gives the percentage of a heavy mineral in the original sample. Since the digestion process described in an earlier section was not completely effective in removing hematite from the samples, figures in Column 1 are calculated from the original modal analysis by eliminating hematite and re-calculating the remaining constituents on the basis of 100 percent. Iron sulfides were also eliminated by calculation where known to be secondary, e.g., in samples from Arkansas.

Arkansas

Six series of three samples, representing syenite, kaolin and bauxite, were collected by the writer. Samples were selected from deposits where the materials appear to be in place. Syenite specimens were mostly collected from outcrops surrounding the deposits, because fresh rock is rarely exposed in mining.

Composite modal analyses of the Arkansas samples are given in Table 1. The heavy minerals in the syenite are ilmenite, rutile, magnetite, and silicates. In the kaolin and bauxite these same minerals occur together with leucoxene and anatase. Some grains are mixtures of ilmenite and leucoxene, ilmenite and anatase, or anatase and leucoxene.

Ilmenite in the syenite occurs in unaltered crystals. In the kaolin and bauxite, some ilmenite is unaltered, but most of it displays various degrees of alteration to secondary titanium oxides (Figs. 1, 2). Alteration of il-

TABLE 1—COMPOSITE MODAL ANALYSES OF THE HEAVY MINERALS IN ARKANSAS BAUXITE

Sample	A-3		A-2		A-1		A-6		A-5		A-4		A-9		A-8		A-7	
Rock type	Syenite		Clay		Bauxite		Syenite		Clay		Bauxite		Syenite		Clay		Bauxite	
% Heavies of sample	5.43		0.06		0.10		5.82		0.84		0.24		9.00		0.17		1.54	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Ilmenite	13.1	0.71	21.06	0.02	6.13	0.01	14.6	0.85	53.00	0.45	3.67	0.01	4.0	0.36	10.97	0.02	34.27	0.53
Leucoxene	—	—	56.03	0.03	61.85	0.06	—	—	20.85	0.17	65.85	0.16	—	—	54.55	0.09	2.89	0.04
Ilmenite-leucoxene	—	—	10.43	0.01	20.79	0.02	—	—	4.35	0.04	16.65	0.04	—	—	15.94	0.03	0.19	Tr.
Anatase	—	—	3.60	Tr.	3.29	Tr.	—	—	0.18	Tr.	11.16	0.03	—	—	15.18	0.03	38.52	0.59
Anatase-ilmenite	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.35	Tr.	12.05	0.19
Anatase-leucoxene	—	—	0.05	Tr.	—	—	—	—	—	—	0.34	Tr.	—	—	0.38	Tr.	—	—
Rutile	—	—	0.07	Tr.	0.22	Tr.	—	—	—	—	0.01	Tr.	0.1	0.01	—	—	—	—
Magnetite	12.1	0.66	—	—	—	—	8.5	0.49	20.75	0.17	—	—	2.9	0.26	0.73	Tr.	11.13	0.17
Silicates	74.7	4.06	8.72	Tr.	7.59	0.01	77.0	4.48	0.86	0.01	2.27	Tr.	92.9	8.36	2.01	Tr.	0.99	0.02
Unidentified	—	—	—	—	0.15	Tr.	—	—	—	—	—	—	—	—	0.02	Tr.	—	—
Totals	99.9	5.43	99.96	0.06	100.02	0.10	100.1	5.82	99.99	0.84	99.95	0.24	99.9	8.99	100.13	0.17	100.04	1.54

Sample	A-12		A-11		A-10		A-13		A-14		A-15		A-16		A-17		A-18	
Rock type	Syenite		Clay		Bauxite		Syenite		Clay		Bauxite		Syenite		Clay		Bauxite	
% Heavies of sample	6.57		0.47		0.98		10.88		1.93		0.95		11.81		0.82		0.48	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Ilmenite	9.3	0.61	77.49	0.36	69.06	0.68	14.3	1.56	0.09	Tr.	0.14	Tr.	4.8	0.57	77.15	0.63	2.12	0.01
Leucoxene	—	—	1.00	0.01	1.27	0.01	—	—	5.56	0.11	5.17	0.05	—	—	1.47	0.01	12.45	0.06
Ilmenite-leucoxene	—	—	1.94	0.01	0.18	Tr.	—	—	0.04	Tr.	—	—	—	—	3.07	0.03	0.37	Tr.
Anatase	—	—	0.58	Tr.	8.03	0.08	—	—	83.18	1.61	76.29	0.72	—	—	—	—	83.23	0.40
Anatase-ilmenite	—	—	—	—	2.68	0.03	—	—	10.71	0.21	16.64	0.16	—	—	—	—	0.07	Tr.
Anatase-leucoxene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rutile	0.1	0.01	0.02	Tr.	0.02	Tr.	—	—	—	—	0.05	Tr.	—	—	0.51	Tr.	0.02	Tr.
Magnetite	4.5	0.30	15.32	0.07	11.08	0.11	2.4	0.26	0.02	Tr.	—	—	1.0	0.11	5.72	0.05	0.07	Tr.
Silicates	85.9	5.64	3.61	0.02	7.80	0.07	83.0	9.03	0.39	Tr.	1.81	0.02	94.0	11.10	12.00	0.10	1.72	0.01
Unidentified	—	—	—	—	—	—	—	—	—	—	0.05	Tr.	—	—	—	—	—	—
Totals	99.8	6.56	99.96	0.47	100.12	0.98	99.7	10.85	99.99	1.93	100.15	0.95	99.8	11.78	99.92	0.82	100.05	0.48

Explanation

Column 1—% of mineral in heavy mineral residues. Column 2—% of minera. in total sample. Tr.—Trace.

Note: Figures in Column 1 calculated after hematite and iron sulfides were eliminated from original modal analyses.

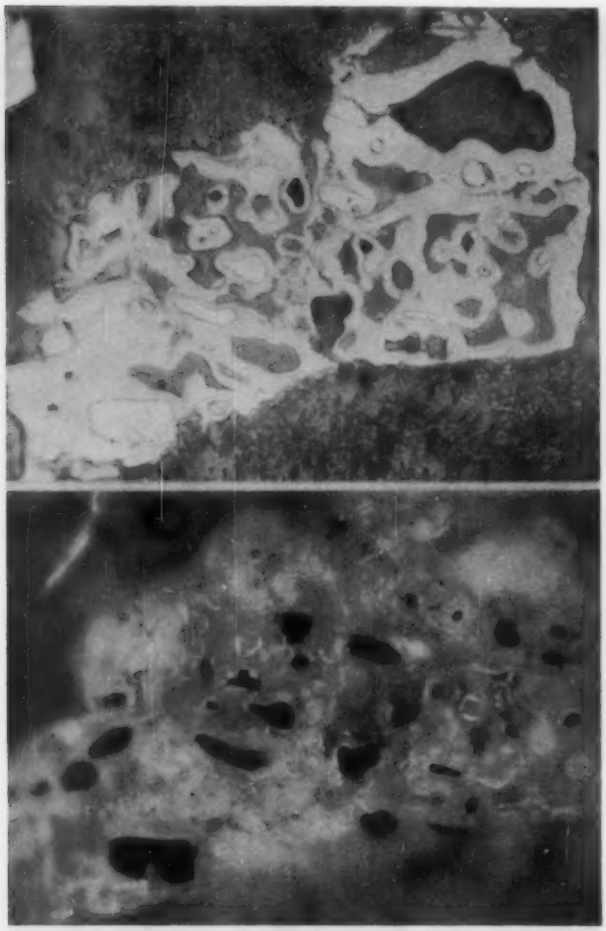

FIG. 1. Anatase type alteration of ilmenite. Note ilmenite residuals. Top, in plain light; bottom, under crossed nicols; ilmenite is opaque, and anatase shows internal reflections. Arkansas. × 155.

menite is discussed in detail in a later section. X-ray fluorescence work on a purified sample of ilmenite shows that it contains manganese in solid solution as indicated by Calhoun (12).

Leucoxene, as used in this study, implies a cryptocrystalline aggregate of secondary titanium oxides, the mineralogical composition of which can be determined only by X-ray methods. The properties of leucoxene in these surfaces vary. Some grains are soft, have moderate reflectivity, and show

internal reflections varying from pure white to light yellowish brown (Fig. 3). Grains of this sort are probably what Bramlette and others have called xanthitane. Other grains have lower reflectivity, are harder, polish poorly and have deep yellowish-brown internal reflections. The differences in

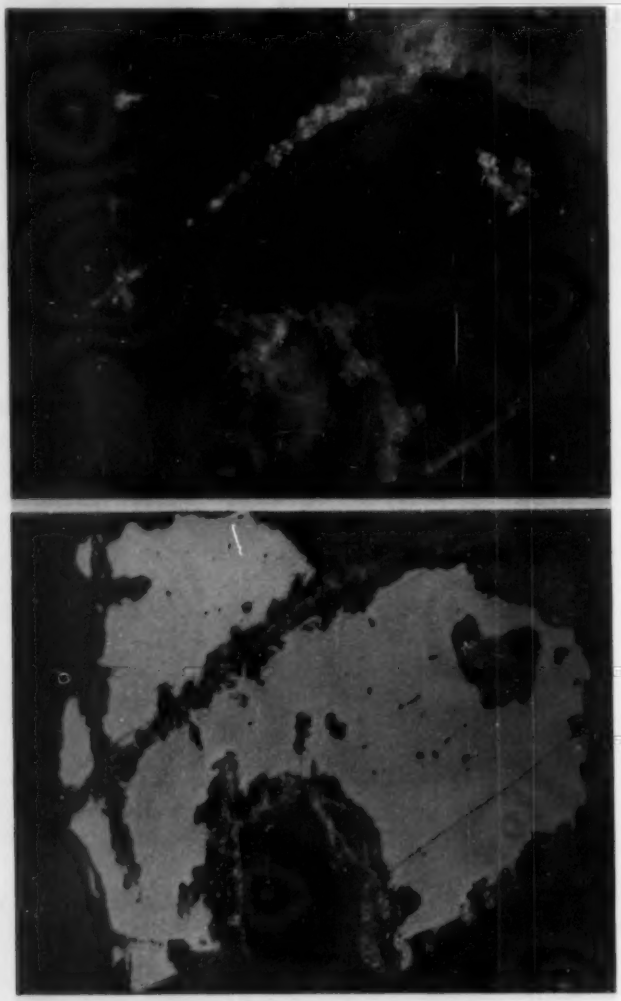

FIG. 2. Early stage of leucoxene replacement of ilmenite. Bottom in plain light, top under crossed nicols. Alteration is proceeding along grain boundaries and along fractures. Arkansas. × 175.

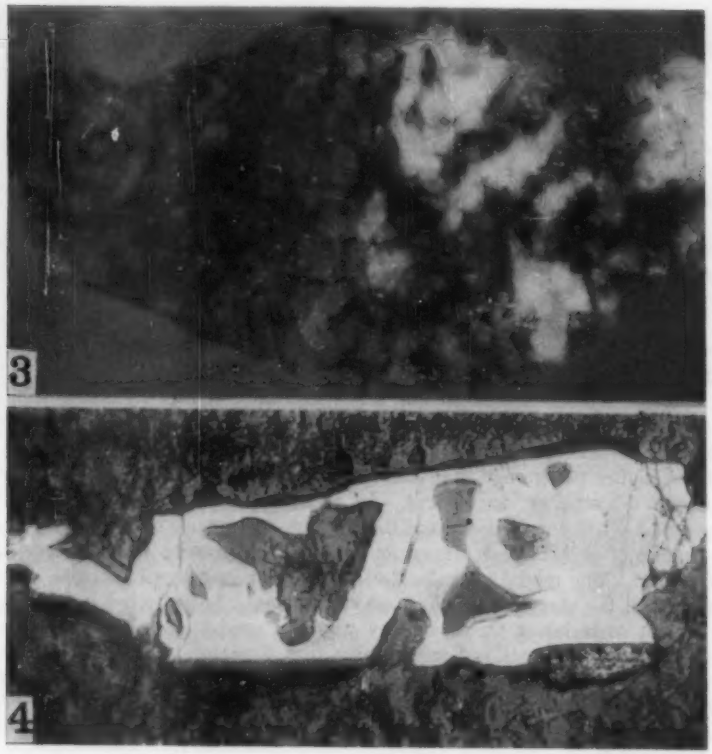

FIG. 3. (Upper.) Leucoxene. Complete alteration of ilmenite. Yellow-brown internal reflections. X-nicols. Arkansas. × 350.

FIG. 4. (Lower.) Complete replacement of ilmenite by anatase. Note platy outline of original ilmenite. Plain light. Arkansas. × 350.

optical characteristics are evidently due to the differences in texture and in the degree of staining with iron oxide, because the X-ray studies described in a subsequent section indicate that either type of leucoxene may consist of anatase or rutile.

Anatase in coarse crystals is not common. It occurs generally as a fine-grained alteration product of ilmenite. The resulting aggregates may retain the platy crystal outline of ilmenite (Fig. 4). Internal reflections of the aggregates vary from pale yellow to moderately deep red. Residual fragments of ilmenite are commonly dispersed throughout anatase found in clays and bauxites of the Arkansas deposits.

Rutile occurs mainly as a constituent of leucoxene grains. Crystalline rutile is present, however, in minor amounts. Its blood red to orange internal reflections distinguish it from anatase.

Table 1 shows that the principal titanium-bearing oxide in the syenites is ilmenite. Thin sections of the syenite, however, show that a certain amount of titanium occurs in sphene, and titanium is probably also present in the ferromagnesian minerals.

Line 3 of Table 1 shows that the + 325 mesh fraction of heavy minerals in Arkansas bauxites and clays accounts for only a small portion of the total sample weight. It therefore appears that the percent of a given mineral in this particular heavy mineral fraction is more significant to this study than the absolute amount of this mineral in the original sample, because the absolute amount will vary due to inhomogeneity of the parent material. With this in mind, the significant figures in the tables are those given in Column 1 for each sample.

In four sets of samples the percentage of unaltered ilmenite is higher in the clay than in the corresponding bauxite. In one other set, represented by A-14 and A-15, the amount of ilmenite is so small both in the clay and in the bauxite that the apparent reversal in percentages may not be significant. In the final set (A-7 and A-8), however, there is a marked difference between the percentage of ilmenite in the clay and the percentage in the bauxite, and the higher percentage is in the bauxite. No obvious explanation of this apparent discrepancy is evident. It seems apparent, however, that the bauxite (A-7) is not derived from the clay (A-8) because of the much greater percentage of + 325 mesh heavy minerals in the bauxite (1.54% compared to 0.17%). The modal analyses do indicate that in general ilmenite is more abundant in the clay than in the bauxite, as would be expected if ilmenite is the parent material of the secondary titanium oxides of + 325 mesh grain size. Polished surfaces indicate clearly that ilmenite is indeed the parent mineral. It is found in all stages of alteration to the various secondary oxides, and there is no indication of oxides formed by alteration of silicates. Any oxides formed by the alteration of silicates must have passed into the − 325 mesh material.

North Ireland

Since no mining of bauxite is being done at the present time, representative samples of Irish ore are difficult to obtain. Two samples of bauxite and one of weathered basalt from the Lyle's Hill deposit and a sample of weathered basalt from Glebe were collected by Dr. E. N. Cameron. No specimens of fresh basalt could be obtained because of lack of exposures. The Glebe sample was not examined. Because of the paucity of heavy minerals coarser than 325 mesh, the two bauxite samples were studied as one specimen. According to Eyles (p. 28 and 34) ilmenite and anatase are present in the Lyle's Hill deposit.

Composite modal analyses of the Irish samples are given in Table 2. Heavy minerals in the altered basalt are ilmenite, leucoxene, anatase, magnetite and silicates. These minerals along with rutile and ilmenite partially altered to leucoxene occur in the bauxite. Descriptions of the minerals given for the Arkansas deposits apply also to the Irish ores except for anatase and part of the leucoxene. Anatase occurs in discrete crystals with internal re-

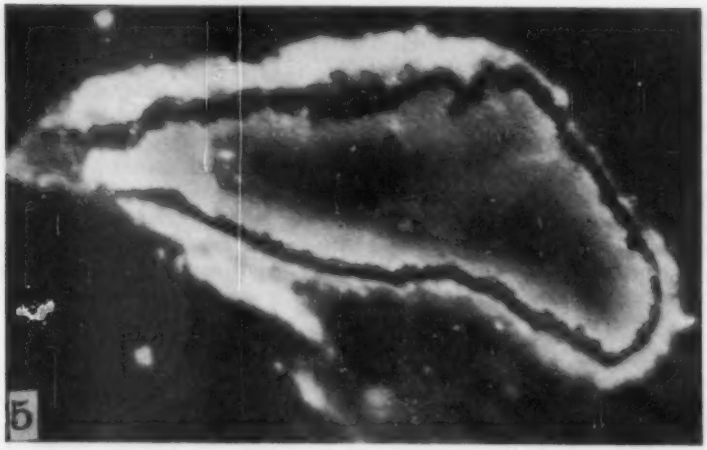

FIG. 5. Leucoxene. X-nicols. Reddish-brown internal reflections. Note ilmenite residuals (opaque). Ireland. × 500.

flections varying from white to light yellow. Anatase is residual from the basalt and is not an alteration product of ilmenite. Some of the leucoxene in the Irish bauxite shows reddish brown internal reflections (Fig. 5). The presence of secondary titanium oxides in the basalt specimen can be attributed to the fact that the sample was not fresh.

Table 2 shows that ilmenite accounts for most of the TiO_2 in the + 325 mesh fraction of the altered basalt, but some TiO_2 probably occurs in the

TABLE 2

COMPOSITE MODAL ANALYSES OF THE HEAVY MINERALS IN IRISH BAUXITE

Sample Rock type % Heavies of sample	I-2 Altered basalt 0.06		I-1 and 3 Bauxite 0.09	
	1	2	1	2
Ilmenite	56.0	0.03	12.69	0.01
Leucoxene	1.5	Tr.	51.28	0.05
Ilmenite-leucoxene	—	—	0.22	Tr.
Rutile	—	—	0.28	Tr.
Anatase	0.3	Tr.	0.08	Tr.
Magnetite	5.9	0.01	2.16	Tr.
Silicates	36.3	0.02	33.40	0.03
Totals	100.0	0.06	100.11	0.09

Explanation

Column 1—% of mineral in heavy mineral residues.
Column 2—% of mineral in total sample.
Tr.—Trace.
Note: Figures in Column 1 calculated after hematite was eliminated from original modal analyses.

silicates. In the bauxite, however, ilmenite is subordinate to the secondary TiO_2 minerals.

Oregon

One series of three samples, consisting of basalt, clay and low-grade ferruginous bauxite, and a specimen of high grade float were obtained from the Salem Hills area. The sample of float was too small to permit a size analysis of the heavy minerals. Apparently the sample of basalt came either from a different flow than that from which the bauxite was derived, or from a different part of the parent flow, because the opaque minerals are much finer in grain than those in the clays and bauxites. They could not be identified at a magnification of 950 ×.

TABLE 3

COMPOSITE MODAL ANALYSES OF THE HEAVY MINERALS IN OREGON BAUXITE

Sample Rock type % Heavies of sample	O-2 Clay 7.17		O-1 Low-grade bauxite 7.36		O-4 Bauxite float 0.05	
	1	2	1	2	1	2
Ilmenite	57.98	4.16	76.43	5.63	83.9	0.04
Leucoxene	0.04	Tr.	1.42	0.10	4.8	Tr.
Ilmenite-leucoxene	—	—	—	—	0.6	Tr.
Rutile	—	—	—	—	0.6	Tr.
Anatase	—	—	—	—	0.4	Tr.
Titaniferous magnetite	22.02	1.58	4.10	0.30	0.7	Tr.
Menaccanite	0.02	Tr.	0.02	Tr.	—	—
Magnetite	19.14	1.37	17.03	1.25	—	—
Iron sulfides	—	—	—	—	0.9	Tr.
Silicates	0.58	0.04	0.95	0.07	7.3	0.01
Unidentified	—	—	—	—	0.6	Tr.
Totals	99.78	7.15	99.95	7.35	99.8	0.05

Explanation

Column 1—% of mineral in heavy mineral residues.
Column 2—% of mineral in total sample.
Tr.—Trace.
Note: Figures in Column 1 calculated after hematite was eliminated from original modal analyses.

Composite modal analyses of the Oregon clay and bauxite are given in Table 3. Both contain the following minerals: ilmenite, leucoxene, rutile, anatase, titaniferous magnetite, menaccanite, iron sulfides, magnetite and silicates. The minerals are similar to those previously described except for titaniferous magnetite and menaccanite. Titaniferous magnetite occurs in appreciable amounts in the clay and low grade ore. It is much less abundant in the float ore. The alteration of this intergrowth in the clay and low-grade ore is peculiar. Ilmenite remains fresh, whereas magnetite is altered to a whitish or brownish substance. This was first believed to be leucoxene but X-ray diffraction patterns indicated only magnetite and ilmenite. On the assumption that the alteration product is of such a grain size that it is amorphous to X-rays, several grains were heated to temperatures of 400° C for

24 to 48 hours, in attempt to anneal them. The X-ray patterns are identical to those taken before heating. Edwards describes a similar alteration product in the bauxites of Tasmania (15). He states that the alteration product is leucoxene, but this has not been confirmed for the material here described.

Unaltered menaccanite, an exsolution intergrowth consisting of lenses of hematite in ilmenite, is found in trace amounts in the clay and low-grade ore.

Table 3 shows that ilmenite is the main titanium mineral in the + 325 mesh fraction even in the float ore. The remarkable feature of this ilmenite is its unaltered condition. One would expect that ilmenite would be progressively more altered with increasing degree of bauxitization but this is not the case. In contrast, Table 3 shows that as bauxitization proceeds, titaniferous magnetite is destroyed. Titanium released during this alteration probably precipitates immediately in oxide particles and passes into the − 325 mesh fractions.

TABLE 4

COMPOSITE MODAL ANALYSES OF THE HEAVY MINERALS IN JAMAICAN BAUXITE

Sample Rock type % Heavies of sample	J-7 Limestone 0.0002		J-2 Bauxite 0.03		J-5 Bauxite 0.01	
	1	2	1	2	1	2
Ilmenite	31.3	Tr.	21.18	0.01	44.74	0.01
Leucoxene	1.3	Tr.	11.52	Tr.	7.19	Tr.
Ilmenite-leucoxene	—	—	17.81	Tr.	11.15	Tr.
Rutile	—	—	2.42	Tr.	0.96	Tr.
Anatase	1.8	Tr.	0.81	Tr.	3.23	Tr.
Titaniferous hematite	1.6	Tr.	1.93	Tr.	1.59	Tr.
Martite	1.8	Tr.	13.66	Tr.	6.14	Tr.
Magnetite	6.0	Tr.	2.60	Tr.	3.00	Tr.
Pyrite	10.4	Tr.	0.22	Tr.	0.23	Tr.
Chalcopyrite	—	—	0.03	Tr.	0.27	Tr.
Silicates	46.0	Tr.	27.73	0.01	21.12	Tr.
Unidentified	—	—	0.08	Tr.	0.05	Tr.
Totals	100.2	Tr.	99.99	0.02	99.67	0.01

Explanation

Column 1—% of mineral in heavy mineral residues.
Column 2—% of mineral in total sample.
Tr.—Trace.
Note: Figures in Column 1 calculated after hematite was eliminated from original modal analyses.

Jamaica

Two samples of bauxite and a composite of two limestone samples were selected from the Belmont area of St. Ann Parish. The Jamaican ores lie directly upon the White Limestone formation (Upper Eocene to Lower Miocene age) without any intervening clay or lithomarge zone.

Composite modal analyses of the samples are given in Table 4. The heavy mineral assemblage in the White Limestone is ilmenite, leucoxene,

TABLE 5

COMPOSITE MODAL ANALYSES OF THE HEAVY MINERALS IN FRENCH BAUXITE

Sample Rock type % Heavies of sample	F-3 Limestone 0.00004		F-4 Clay 0.02		F-5 Bauxite 0.02		F-1 Bauxite 0.05		F-2 Bauxite 0.23	
	1	2	1	2	1	2	1	2	1	2
Ilmenite	13.7	Tr.	0.65	Tr.	0.27	Tr.	46.02	0.02	0.86	Tr.
Leucoxene	8.8	Tr.	2.78	Tr.	42.71	0.01	6.06	Tr.	25.67	0.06
Ilmenite-leucoxene	—	—	—	—	—	—	0.03	Tr.	—	—
Anatase	3.1	Tr.	1.76	Tr.	9.99	Tr.	0.99	Tr.	4.58	0.01
Rutile	4.1	Tr.	0.59	Tr.	4.67	Tr.	2.08	Tr.	11.65	0.03
Magnetite	31.1	Tr.	0.53	Tr.	1.28	Tr.	14.40	0.01	0.18	Tr.
Chalcopyrite	—	—	0.31	Tr.	—	—	—	—	0.13	Tr.
Silicates	38.9	Tr.	93.23	0.02	41.52	0.01	30.70	0.02	56.82	0.13
Totals	99.7	Tr.	99.85	0.02	100.44	0.02	100.28	0.05	99.89	0.23

Explanation

Column 1—% of mineral in heavy mineral residues.
Column 2—% of mineral in total sample.
Tr.—Trace.
Note: Figures in Column 1 calculated after hematite was eliminated from original modal analyses.

anatase, titaniferous hematite, martite, magnetite, sulfides and silicates. In the bauxite the heavy minerals found in the White Limestone occur together with rutile and aggregates of ilmenite and leucoxene. In general, the heavy minerals are similar in characteristics to those described in previous sections. Titaniferous hematite occurs in the two forms previously described by Hartman (24). In this earlier paper the intergrowth was reported from the bauxite but not from the limestone. Martite is formed by the complete oxidation of iron in magnetite. It occurs in dense crystalline aggregates. Sulfides consist of pyrite and chalcopyrite. Only the former mineral was found in the limestone.

Examination of Table 4 shows that unaltered ilmenite is an important constituent in both the limestone and the bauxite. Secondary titanium oxides, however, are abundant only in the bauxite. Sample J-5 contains more ilmenite than the limestone. This is probably the result of local concentrations of heavy minerals in the bauxite because the ore has been transported for a short distance.

France

Two isolated samples of bauxite and a series of three samples consisting of limestone, clay and bauxite were obtained from France. The French ores consist chiefly of boehmite, and for this reason are difficult to digest.

Composite modal analyses of these surfaces are given in Table 5. The limestone contains the following heavy minerals: ilmenite, leucoxene, anatase, rutile, magnetite and silicates. In addition to these, the clay and bauxite contain chalcopyrite and composite grains of ilmenite and leucoxene. The minerals are similar in characteristics to those described earlier in this paper.

Table 5 shows that the limestone contains appreciable amounts of crystal-

line anatase and rutile. These minerals resist alteration during bauxitization. French bauxites contain a greater percentage of crystalline rutile and anatase in the heavy residues than any other samples examined.

In the sequence of three samples (F-3, F-4, F-5) ilmenite is most abundant in the limestone and least abundant in the bauxite. The content of ilmenite in sample F-2 is slightly higher than that of the clay (F-4) but less than that of the limestone, whereas in sample F-1 ilmenite is more abundant than in the limestone represented by sample F-3. These discrepancies can reasonably be explained by variation in the source rock, since the bauxites represented by F-1 and F-2 come from a different area than the sequence F-3, F-4 and F-5. Minor local transportation during bauxitization might also be a factor.

Surinam

Samples from the Rorac district and from Paranam were sent to the writer by Dr. Wilson D. Michell. Two specimens, cellular white bauxite and underlying clay, were selected from Paranam. The Rorac group was not examined because all the samples were bauxite.

Composite modal analyses of the Surinam samples are given in Table 6. The heavy minerals in the kaolin and bauxite are ilmenite, leucoxene, rutile, anatase, magnetite, iron sulfides, and silicates. Aggregates of ilmenite and leucoxene are also found. The minerals appear identical to those previously described.

Table 6 shows that the clay and bauxite contain an abundance of the secondary titanium oxides and very little ilmenite. Since the nature of the source material of the clay is not known, it is not possible to determine

TABLE 6

COMPOSITE MODAL ANALYSES OF THE HEAVY MINERALS IN SURINAM BAUXITE

Sample Rock type % Heavies of sample	S-4 Clay 0.14		S-2 Bauxite 0.01	
	1	2	1	2
Ilmenite	1.39	Tr.	1.56	Tr.
Leucoxene	67.82	0.10	66.68	0.01
Ilmenite-leucoxene	0.12	Tr.	—	—
Rutile	1.21	Tr.	0.18	Tr.
Anatase	0.96	Tr.	1.01	Tr.
Magnetite	0.05	Tr.	—	—
Iron sulfides	0.03	Tr.	0.32	Tr.
Silicates	28.30	0.04	30.36	Tr.
Unidentified	0.07	Tr.	—	—
Totals	99.95	0.14	100.11	0.01

Explanation

Column 1—% of mineral in heavy mineral residues.
Column 2—% of mineral in total sample.
Tr.—Trace.
Note: Figures in Column 1 calculated after hematite was eliminated from original modal analyses.

whether the alteration of ilmenite occurred in the source rock in situ, during transportation of sediment from the source, or at its present site.

X-RAY STUDIES

General Statement.—X-ray diffraction studies were made in order to determine the mineralogical composition of leucoxene and to determine the distribution of the polymorphs of TiO_2 in bauxite and associated clay. Three grains of leucoxene were selected from either the $-40+100$ or the $-100+140$ fraction of each sample and diffraction patterns were obtained from these grains. A detailed examination was made on samples A-4 (bauxite) and A-5 (clay). Fifty leucoxene grains from each sample were removed from the polished surface. Each grain was mounted on the end of a glass fiber and X-rayed. One sample of ilmenite and one of anatase, each cleaned of other minerals as completely as possible, were studied by X-ray fluorescence to determine the impurities in each.

TABLE 7

RESULTS OF X-RAY DIFFRACTION STUDIES

Sample No.	Location	Rock Type	Grain 1	Grain 2	Grain 3
A-1	Arkansas	Clay	A	R	A
A-2	Arkansas	Bauxite	R	R	R + A
A-4	Arkansas	Bauxite	A	R	A + R
A-5	Arkansas	Clay	A	A	A
A-7	Arkansas	Bauxite	A	A	A
A-8	Arkansas	Clay	R + A	R + A	R
A-10	Arkansas	Bauxite	A	A	A
A-11	Arkansas	Clay	A + R	A	A
A-14	Arkansas	Clay	A	A	A
A-15	Arkansas	Bauxite	A	A	A
A-17	Arkansas	Clay	A + R	A + ?	A + R
A-18	Arkansas	Bauxite	A	A	R
I-2	Ireland	Altered basalt	A + R	R	A
I-1 & 3	Ireland	Bauxite	R	R	R
S-2	Surinam	Bauxite	R	R	R
S-4	Surinam	Clay	R + A	R	R
F-1	France	Bauxite	R	A + R	A
F-2	France	Bauxite	R	R + A	R + A
F-3	France	Limestone	R + A	R	R + A
F-4	France	Clay	R	R	A + R
F-5	France	Bauxite	R	R	A
J-2	Jamaica	Bauxite	R	R + A	R
J-5	Jamaica	Bauxite	R	R	R
O-1	Oregon	Clay	A	A	A
O-4	Oregon	Bauxite	R	A	R

Explanation

A—Anatase.
R—Rutile.

Results of Diffraction Studies.—Table 7 gives results of the diffraction study of the three grains of leucoxene in each bauxite and clay sample. Table 8 summarizes results given in Table 7. Examination of these tables shows

TABLE 8

SUMMARY OF THE DISTRIBUTION OF THE TiO_2 POLYMORPHS IN THE CLAYS AND BAUXITES[1]

District	Clay			Bauxite		
	A	R	A + R	A	R	A + R
Arkansas	10	2	6	12	4	2
Ireland[2]	1	1	1	—	3	—
Oregon	3	—	—	1	2	—
France	—	2	1	2	4	3
Jamaica[3]	—	—	—	—	5	1
Surinam	—	2	1	—	3	—
Totals	14	7	9	15	21	6

Note

[1] The numbers in this table refer to the number of times each polymorph was identified in X-ray studies reported in Table 7.
[2] The "clay" sample is actually weathered basalt.
[3] No clay horizon associated with Jamaican bauxite.

Explanation

A—Anatase.
R—Rutile.

that rutile and anatase occur in both bauxite and clay. The relative percentages of rutile and anatase in the grains listed in Tables 7 and 8 are given below:

	Clay	Bauxite
Anatase	47	36
Rutile	23	50
Anatase + rutile	30	14
Total	100%	100%

In order to determine if one polymorph is more abundant in clay as compared to bauxite, samples A-4 and A-5 from Arkansas were studied in detail. The results are most interesting as given in Table 9. All fifty grains of leucoxene from the clay consist of anatase. In the bauxite thirty grains consist of rutile, eight grains consist of anatase and twelve grains are rutile-anatase mixtures. This detailed study suggests that anatase is the common TiO_2 polymorph in the clay and that rutile occurs mainly in the bauxite. Similar studies of a number of sets of samples would be required, however, to establish this as the general rule in the Arkansas district.

It is interesting to note that the X-ray work did not indicate the presence of brookite. This is surprising, especially for the Arkansas deposits, because

TABLE 9

RESULTS OF X-RAY DIFFRACTION STUDY OF SAMPLES A-4 AND A-5

Sample No.	Rock Type	Anatase	Rutile	Rutile + Anatase	Brookite
A-4	Bauxite	8	30	12	nil
A-5	Clay	50	nil	nil	nil

Frederickson (18) reported that brookite is the main alteration product of ilmenite in the core he studied.

Results of Fluorescence Studies.—Anatase from sample A-14 and ilmenite from sample A-17 were studied by fluorescence techniques to determine the impurities in each. The impurities present, each indicated by an "x," are given below:

Sample	Mineral	Mn	Cb	Zr	Fe
A-14	Anatase	nil	x	x	x
A-17	Ilmenite	x	x	nil	

Mn substitutes for Fe in ilmenite. Cb substitutes for Ti in anatase and in ilmenite. Zr is probably present as zircon rather than in the lattice of anatase. The amount of substitution of Fe for Ti in anatase is not known because Fe is present in part in residual ilmenite.

Fleischer et al. (17) and Gordon and Murata (22) concluded that in Arkansas bauxite Cb occurs in larger amounts in ilmenite than in the three polymorphs of TiO_2. For the material studied the reverse appears to be true because a higher peak for Cb was obtained on the graph of anatase. One would expect this to be true since anatase is an alteration product of ilmenite. The Cb ions present in ilmenite probably become incorporated in the anatase lattice during the process of alteration of ilmenite to anatase. Since Fe is leached from ilmenite during alteration to anatase and since most of the Cb and Ti remain in situ, the percentage of Cb in the alteration product, i.e., anatase, would necessarily be higher than in parent ilmenite. A minor amount of Cb probably precipitates as finely divided particles of Cb_2O_5 which would pass through the − 325 sieve used for this study.

In one sample of brookite from Arkansas bauxite Frederickson (18) found that the impurities are Fe, Zr, Al, Ca, and Si. He believes that the first two elements substitute for Ti and that the latter three elements suggest that titanite was present. He does not state whether the content of Cb was determined.

In the alteration of ilmenite Mn does not enter into the lattice of anatase. This is a consequence of the difference in ionic radii of Ti and Mn. Mn released during alteration of ilmenite is probably dispersed in fine manganese dioxide particles of − 325 grain size.

INTERPRETATION OF RESULTS

General Statement.—Data given in the preceding sections must be interpreted in terms of the origin of bauxite deposits. Origin by weathering was proposed by Mead for the Arkansas deposits (33), and his theory went unchallenged for almost three decades. Mead concluded that kaolin is the initial alteration product of the syenite and that bauxite is formed by desilication of kaolin. During World War II geologists of the U. S. Geological Survey reexamined the Arkansas deposits, and Gordon, Goldman and Tracey (21, 23) subsequently attempted to prove that Mead's theory is incorrect.

These authors agree that the bauxite is a residual product of the syenite. They contend, however, that bauxite is a direct alteration of syenite and that kaolin is a product of resilication of bauxite. Field observations indicate that some resilication of bauxite has occurred, but in the present writer's opinion, Goldman, Gordon and Tracey have failed to prove that resilication of bauxite is a widespread phenomenon.

The spatial relationship of parent rock-clay-bauxite for the deposits of France, Surinam, Ireland and Oregon is identical to that of Arkansas. Jamaican ores lie directly on limestone, however, without the intervening clay horizon found in other districts. Since the majority of bauxite deposits are believed to have formed in the manner described by Mead, his theory will be followed in the interpretation of the results of this study.

TABLE 10

TITANIUM MINERALS IDENTIFIED IN THE SOURCE ROCKS, CLAYS, AND BAUXITES STUDIED

	Ilmenite	Leucoxene	Rutile	Anatase	Titaniferous hematite	Titaniferous magnetite	Menaccanite
Source Rocks:							
Arkansas	x						
Oregon	x					x	x
Ireland	x			x			
Jamaica	x	x		x	x		
France	x	x	x	x			
Surinam[1]	x	x	x	x			
Clays:							
Arkansas	x	x	x	x			
Oregon	x	x				x	x
Ireland[2]	x	x		x			
Jamaica[3]							
France	x	x	x	x			
Surinam	x	x	x	x			
Bauxites:							
Arkansas	x	x	x	x			
Oregon	x	x	x	x		x	x
Ireland	x	x	x	x			
Jamaica	x	x	x	x	x		
France	x	x	x	x			
Surinam	x	x	x	x			

Note

[1] Assuming the transported clays are the source.
[2] "Clay" is actually partially altered basalt.
[3] No clay horizon in Jamaica.
"x" denotes identification.

Titanium Mineralogy of + 325 Mesh Fraction of Samples Studied.—Tables 1 to 6 show that relative amounts of minerals in the + 325 mesh fraction of heavy minerals vary widely from district to district. Table 10 shows, however, that the assemblage of titanium minerals in bauxites is almost identical in the various districts. The following exceptions are noted. Titaniferous hematite occurs only in the Jamaican ores, and titaniferous magnetite

and menaccanite were found only in samples from Oregon. The alteration of ilmenite to optically identifiable, fine-grained anatase was observed only in Arkansas bauxite.

The general similarity in secondary mineral assemblages is remarkable. It would be reasonable to expect that the chemical environments produced by the weathering of these diverse source rocks would differ, and that this would be reflected in differences in the titanium minerals developed. Apparently this is not the case. Only in Arkansas is there evidence of a variation in the products which are produced during alteration of ilmenite.

As bauxitization proceeds the degree of alteration of ilmenite generally increases. Secondary oxides are generally more abundant in the bauxites than in the clays. In the Oregon samples, however, ilmenite resists alteration even in the high-grade float ore. In sample A-7 from Arkansas ilmenite is more abundant than in the underlying clay. It is uncertain whether these variations are related to an original difference in parent rock, to the composition of the solutions responsible for the alteration, or some other factor.

Soil scientists have maintained for some time that residues derived from variable source rocks under similar climatic conditions will be similar (10, 28, 40, 41). Geologists (e.g., 36) have thought that parent rock influences the composition of the residues to some degree. The results of this study tend to support the conclusions of the soil scientists. Local factors, of which character of parent material may be one, must be called upon, however, to account for the variations described above.

Tables 1–6 show that the + 325 mesh fraction accounts for only a part of the TiO_2 in these bauxites. The remainder, and commonly the larger percentage, of the TiO_2 must occur in material finer than 325 mesh. Part of the TiO_2 in this size range comes from the alteration of ilmenite, and part comes from weathering of titanium-bearing silicates.

Alteration of Titanium Minerals During Formation of Bauxite.—For the purposes of the present study the significant titanium minerals present in the source rocks of bauxite from the various districts (Table 10) are the oxide minerals ilmenite, anatase, rutile, leucoxene, titaniferous hematite, menaccanite and titaniferous magnetite. The presence of leucoxene in the source rocks suggests that these samples were not entirely fresh because leucoxene is not a primary mineral. Sphene and other titanium-bearing silicates are also present in source rocks of the Oregon, Ireland and Arkansas deposits, but the products of alteration of these minerals evidently pass into the − 325 mesh fraction and are not within the scope of the investigation. Of the oxide minerals, anatase, rutile, leucoxene, titaniferous hematite and menaccanite remain unchanged during alteration. The alteration of titaniferous magnetite, discussed in a previous section, is obscure. We are concerned, therefore, largely with the alteration of ilmenite, which is not only susceptible to alteration during bauxitization, but is by far the most abundant source oxide of titanium in all the districts.

Alteration of ilmenite grains in beach sands has been studied by Bailey, Cameron, Spedden, and Weege (2) and Lynd, Sigurdson, North and Anderson (32). Bailey et al. found that alteration proceeds through three stages.

First is a patchy alteration to amorphous iron-titanium oxide along grain boundaries, along fractures in the grains or along parallel bands believed to represent the traces of the basal parting of ilmenite. Complete alteration results in the second or amorphous stage. During the third stage the amorphous material recrystallizes to finely crystalline TiO_2 (leucoxene). Commonly all three stages are found in a single grain, but the above sequence is maintained. X-ray diffraction patterns of selected grains indicate that the leucoxene consists largely of rutile, but brookite has also been found, and further study by Bailey and Cameron (3) has shown that anatase may be present.

Alteration of ilmenite during bauxitization does not proceed in the same manner as described by Bailey et al. for beach sands. At least three types of alteration were observed under the microscope: 1) direct alteration to leucoxene; 2) direct alteration to optically identifiable anatase; 3) alteration to a patchy ilmenite similar to stage 1 in beach sands. All three of the above alteration products occur in the Arkansas deposits; in the other deposits examined, however, only direct alteration of ilmenite to leucoxene was seen.

Direct replacement of ilmenite by leucoxene is the most common type of alteration. Contacts between the two substances are sharp. In beach sands (2, p. 265) the initial stage of alteration of ilmenite is commonly controlled by the crystal lattice of ilmenite. In bauxites no grain showing such relationships has been observed. Instead, alteration proceeds from the edge of the grain, or from fractures (Fig. 2), until ilmenite is completely replaced by leucoxene (Fig. 3). All stages of this alteration can be observed under the microscope. X-ray studies show that leucoxene may consist of either anatase or rutile, but the aggregates are too fine-grained for optical identification.

In the second type of alteration certain ilmenite grains are replaced by fine-grained aggregates of anatase that have light yellow to moderately deep red internal reflections. Alteration of this type is generally in an advanced stage, so that residual ilmenite occurs only in small isolated remnants surrounded by anatase (Fig. 1). In some grains ilmenite has been completely replaced by anatase (Fig. 4). Contacts between ilmenite and anatase are sharp, and no amorphous zone is present between the two.

The third type of alteration is similar to the patchy stage in the beach sands. A few grains of this type were seen in Arkansas bauxite, but not in the other bauxites.

The detailed X-ray diffraction study of samples A-4 and A-5 shows that anatase is more abundant in the clay (A-5) and that rutile is more abundant in the bauxite (A-4). In anatase the bond angle between adjacent titanium ions lying in a common plane is not 90°, but in rutile this angle is 90° (6). Because of the uneven distribution of its titanium ions, anatase should be less stable than rutile. This may explain why the stability sequence of the TiO_2 polymorphs, from most stable to least stable, is rutile, brookite and anatase. The stresses produced by the non-uniform distribution of the titanium ions in anatase could be dissipated by re-orientation of the titanium ions into the more stable configuration of rutile. It seems probable that time would favor

this re-orientation, and since the bauxite (A-4) is derived from the clay (A-5) rutile should be more abundant in the bauxite.

In view of the lack of information on the geochemistry of titanium the conditions under which the alteration of ilmenite occurs can be only roughly surmised from the chemistry of the other constituents in bauxites. The major constituents in bauxites are Al_2O_3, Fe_2O_3, SiO_2, and TiO_2. Al is stable in the pH range of 4 to 10. Fe is soluble only in acid solutions. Si is slightly soluble in acid solutions but its solubility increases rapidly with rising pH. In the formation of bauxite silica is the major constituent leached, but Mead showed that in Arkansas iron is also partially removed during bauxitization. To resolve what seemed to be a paradoxical situation in which solutions must be alkaline to effectively remove silica and acid to leach iron, some authors (5, p. 215 and others) have called upon alternating wet and dry seasons to cause the pH of solutions to fluctuate from acid to alkaline. In Hawaii, however, Sherman (38, p. 312) reports that bauxite is forming today in areas that have a continuous wet season and in which the ground water is acid.

In view of the work by Sherman it would appear that bauxite may form under mildly acid conditions. However, one is not justified in assuming that all bauxite deposits are formed by acid solutions. We can therefore set only wide limits on the formation of bauxites based on the stability of aluminum in the pH range of 4 to 10.

Size Range of the Secondary Titanium Minerals.—Modal analyses of the size fractions show that in general the titanium minerals coarser than 325 mesh are concentrated in one of two size ranges, $-40+100$ and -200 mesh. Exceptions occur but they are not common. Bauxites derived from syenites and non-calcareous sediments show maxima in both of the above size ranges, whereas bauxites developed from basalt and especially those accumulating on limestones commonly show a maximum in the -200 fraction. These variations in grain size are probably related to the origin of the parent rocks of the bauxite deposits.

The individual crystallite size of the TiO_2 polymorphs in leucoxene can be estimated from the X-ray diffraction patterns. X-ray patterns of leucoxene consisting of anatase commonly show regular, continuous lines; most rutile patterns appear spotty. This indicates that anatase is finer grained than rutile, and that its grain size is on the order of 10^{-4} cm.

Mineralogical Composition of Leucoxene.—The mineralogical composition of leucoxene has been a subject of controversy for many years. A chemical analysis of leucoxene invariably shows the presence of Fe_2O_3. The controversy revolves around the position of Fe_2O_3. The Fe^{+3} ion may replace the Ti^{+4} ion in the crystal lattice or Fe_2O_3 and TiO_2 may be an intimate mechanical mixture. Arizonite, having a chemical composition of $Fe_2O_3 \cdot TiO_2$, was first described by Palmer (35) in 1909. Although the evidence for the existence of arizonite is scanty, this term has become deeply entrenched in the geological literature (4, 19, 20, 34). Recent studies by Cannon (13), Lynd et al. (32) and Bailey and others (2) present convincing evidence that arizonite does not occur in beach sands.

In the present study almost 200 X-ray photographs of leucoxene aggregates were taken. All of the patterns match either anatase or rutile. The extra lines or spots present on some of the photographs commonly coincide with the strong lines of ilmenite. The presence of arizonite was not detected in any bauxite or clay sample. The internal reflections of leucoxene are commonly a yellow brown. This hue is believed to be a function of the content of iron oxide mechanically mixed with TiO_2 in the leucoxene grain (2). Chemical analysis of some of the aggregates with yellow-brown internal reflections would probably yield results that would agree with the hypothetical formula for arizonite. Bramlette's analysis of "xanthitane" shows Fe_2O_3 (7, p. 17).

Factors Controlling the Formation of TiO_2 Polymorphs.—Numerous experiments have been undertaken to determine the stability fields of the TiO_2 polymorphs. It has been shown, for example, that anatase transforms to rutile at about 900° C (39). In the synthesis of the polymorphs of TiO_2 Brammell and Harwood (8) found that anatase formed at the lowest temperature, brookite at a somewhat higher temperature and rutile at a considerably higher temperature. The results of these experiments are of no value to the present study because the temperatures employed greatly exceed what one would expect in weathering. Moreover, Ingerson (27, p. 353) points out that anatase and brookite are monotropic with rutile. Therefore, factors other than heat must play the dominant role in determining which TiO_2 polymorph will form during the alteration of ilmenite under surface or near-surface conditions, because secondary rutile, anatase and brookite all occur in bauxite deposits.

The crystal chemistry of the polymorphs of TiO_2 is discussed by Huckel (25). According to Huckel anatase is least stable, brookite is intermediate in stability and rutile is the most stable of the three polymorphs. Factors that control polymorphism at low temperatures are imperfectly understood at the present time. It is possible to speculate, however, that any one or a combination of the following factors may determine which polymorph of a given substance will occur: temperature, pressure, polarization, pH, rate of alteration, or impurities. The first three factors are not important for the present study.

The pH of the solutions responsible for the alteration of parent material to bauxite must lie between 4 and 10. These same solutions must be responsible for the alteration of ilmenite. Minor variations in pH within this range might cause the stability fields of the polymorphs to shift. Until more experimental data are available, however, it is not possible to state which polymorph is stable at a given pH in this range.

The rate of alteration of ilmenite to secondary titanium oxides might control the formation of a polymorph. If alteration is rapid and occurs at low temperature the titanium ions might not become oriented in the most stable sites. As the mineral ages, however, the ions would assume a more stable configuration. Considering the polymorphs of TiO_2, anatase should then revert to rutile.

The effect of impurities on the formation of polymorphic forms has been examined by many workers. It has been shown that impurities determine which polymorph of $CaCo_3$ will precipitate from the solution (43). The stabilizing effect of impurities on cristobalite has been noted (11). Schossberger (37) has conducted experiments on the precipitation of TiO_2 from acid solutions. He found that precipitation from an H_2SO_4 solution produced anatase and that precipitation from an HCl solution produced rutile. Upon adding 5 percent by weight of H_2SO_4 to the HCl solution Schossberger was able to precipitate anatase. He concluded, using X-ray techniques and density measurements, that anatase was stabilized by SO_3 in the crystal lattice. Schossberger suggested that brookite is stabilized by some unknown impurity. Frederickson showed that iron and zirconium occur in the brookite from Arkansas bauxites. The present study shows that anatase contains columbium and possibly iron in its lattice. Unfortunately, a sample of rutile cannot be readily obtained from Arkansas bauxites, so that a comparison of the impurities cannot be made. It is evident from the work of Schossberger, however, that impurities are important in determining which polymorph of TiO_2 will form at low temperature.

APPRAISAL OF ECONOMIC POTENTIALITIES OF BAUXITE RESIDUES AS A SOURCE OF TiO_2

Bauxites are treated by the Bayer process in order to recover Al. Because the digestion process is carried out under strongly alkaline conditions, Fe and Ti oxide minerals remain inert and consequently pass into the tailings. Minerals present in the tailings are the Fe and Ti minerals of bauxites together with undissolved quartz in the ore and sodium aluminum silicates formed during digestion. Hence, the TiO_2 tenor of the bauxite tailings is considerably above that of beach sands mined in the United States at the present time. If the titanium minerals are coarse enough so that a simple gravity concentration method can be employed and if alteration of ilmenite has proceeded sufficiently so that a high grade concentrate can be obtained, bauxite tailings could be used as an ore of titanium.

This study shows that the residues from some of the districts contain an appreciable amount of TiO_2 in the + 325 fraction. Of the ores studied those from Arkansas appear to be the most amenable to treatment. Alteration of ilmenite has proceeded in most ore bodies to an advanced stage, and the grain size of the secondary titanium oxides is coarse when compared to the other districts.

The other five districts do not appear to be of potential economic interest because ilmenite is unaltered or because the titanium oxides are too fine-grained. Although the French ores contain crystalline rutile and anatase, these minerals are for the most part in the − 200 fraction and would be difficult to recover. If the metallurgist develops a method for the recovery of titanium from fine-grained mixtures of titanium minerals and other minerals, all bauxite districts will then become potential sources of titanium ore.

CONCLUSIONS

1. The titanium minerals found in the bauxites and clays studied are rutile, anatase, leucoxene (finely crystalline TiO_2, either rutile or anatase), ilmenite, titaniferous magnetite, menaccanite and titaniferous hematite. The first four minerals are common to all deposits regardless of the variation in source rock. Titaniferous hematite, titaniferous magnetite and menaccanite are very limited in distribution. The bulk of the anatase and all of the leucoxene are secondary, and forms as alteration products of ilmenite. Titanium occurring in silicates in the parent rock is probably responsible for most of the titanium in the -325 mesh material.

2. Ilmenite is the principal parent mineral for the secondary titanium oxides of $+325$ mesh grain size in the bauxites studied. Grains of ilmenite are observed in all stages of alteration to secondary oxides.

3. Alteration of ilmenite in bauxites varies from that reported in beach sands. Three types of alteration occur: 1) alteration to leucoxene; 2) alteration to optically identifiable anatase; and 3) alteration to a patch-type ilmenite in which part of the grain is altered to an amorphous iron-titanium oxide. Type 3 is similar to the patchy stage found in beach sands. Type 1 is found in all deposits; types 2 and 3 occur only in Arkansas bauxite.

4. The detailed X-ray diffraction study of samples A-4 and A-5 from Arkansas suggests that at least for these deposits, anatase is the initial alteration product of ilmenite. Additional detailed work on all deposits is required in order to confirm this suggestion.

5. Inasmuch as the polymorphs of TiO_2 in bauxites and associated clays are the same regardless of the type of parent material, it appears that the parent rock exerts little if any influence in determining which polymorph will form. The parent rock, however, has some effect on the size of the titanium minerals in the bauxites. In materials examined, ores derived from syenites and non-calcareous sediments show a maximum in either the $-40 + 100$ or -200 mesh fractions; bauxites formed on limestones and basalts show a maximum in the -200 mesh fraction.

6. Leucoxene in the bauxites and associated clays consists of rutile and anatase. Almost 200 X-ray diffraction patterns failed to disclose any other TiO_2 mineral except the occasional appearance of the strong lines of parent ilmenite. No evidence was obtained indicating that arizonite is present in these samples.

7. In general the bulk of the TiO_2 in bauxites occurs in the -325 mesh fraction. Three samples of bauxite from Arkansas, however, show appreciable amounts of TiO_2 in the $+325$ mesh material.

8. Factors that control the formation of TiO_2 polymorphs under surface conditions are not known at the present time. Temperature, pressure and polarization cannot be important. Rate of alteration, pH and impurities may be major factors in determining which polymorph will form.

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THE GEOCHEMISTRY OF RHENIUM, WITH SPECIAL REFERENCE TO ITS OCCURRENCE IN MOLYBDENITE[1]

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ABSTRACT

Little has been added to our knowledge of the geochemistry of rhenium since the work of Noddack and Noddack (16) in 1931, except that many determinations have been published of the rhenium content of molybdenite, the only present source. These determinations, 150 in all, have been assembled. The rhenium content of molybdenite ranges from none to 3,250 ppm Re, and varies widely, even in samples from a single deposit. No generalizations are yet possible as to correlations of rhenium content with geological conditions of formation. Other possible sources of rhenium are considered briefly.

INTRODUCTION

RHENIUM, the element of atomic number 75, is one of the rarest of the chemical elements and was not discovered until 1925, although many previous investigators had claimed proof of finding it. The history of these studies is summarized by Druce (7).

Rhenium is placed in Column 7B of the periodic table of elements below manganese and technetium; the latter element has not yet been proved to exist in nature. Rhenium in the periodic table is adjacent horizontally to tungsten and to the platinum metals and diagonally to molybdenum; it might therefore be expected to show some geochemical associations with manganese, tungsten, the platinum metals, and molybdenum. In fact, the association with molybdenum is marked; there is evidence of only a slight degree of association with manganese, the platinum metals, and tungsten.

Chemically, rhenium is known in the valence states -1, $+1$, $+2$, $+3$, $+4$, $+5$, $+6$, and $+7$; of these, the $+4$ and $+7$ states are the most stable and the most important. The ionic radii are given by Ahrens (1) as Re^{+4} 0.72, Re^{+7} 0.56 A; these may be compared with Mo^{+4} 0.70, W^{+4} 0.70, Mn^{+4} 0.60, Mo^{+6} 0.62, W^{+6} 0.62 A. From these it would be reasonable to expect that rhenium could be associated with quadrivalent molybdenum and tungsten and, to a lesser degree, with quadrivalent manganese. It is probably true that size of ionic radius has little to do with the possible entry of rhenium into the minerals molybdenite and tungstenite, in which the bonding is covalent; however, ReS_2 has a crystal structure very similar to those of MoS_2 and WS_2. Surveys of the literature on rhenium have recently been published (21, 23).

[1] Publication authorized by the Director, U. S. Geological Survey. Paper presented at the meeting of the A.I.M.E., Los Angeles, May 1958.

RHENIUM IN ROCKS AND METEORITES

Our present knowledge of the geochemistry of rhenium rests almost entirely on the work of Ida and Walter Noddack (16), with the exception of new analyses of molybdenite and a few other determinations mentioned later. These investigators state that they analyzed some 1,600 samples of minerals and rocks, but they actually published analyses of only 220 samples, in many of which rhenium was not found. The abundance of rhenium in the Earth's crust, given in nearly all reference works as 0.001 ppm, is based on a single determination by the Noddacks on a composite sample of 110 igneous rocks. One is tempted to speculate that this value may be one or two orders of magnitude too low, as seems to be true for their data on meteorites discussed below. Vinogradov (25) quotes unpublished work by Basitova [2] as giving 0.06 ppm Re in basic rocks and 0.006 ppm Re in acidic rocks, yielding an average of about 0.01 ppm, which is one order of magnitude higher than the Noddacks' figure.

The data on meteorites are given in Table 1. The recent determinations are two orders of magnitude higher than the Noddacks'.

TABLE 1

RHENIUM CONTENT OF METEORITES IN PARTS PER MILLION

		Reference
Iron meteorites (avg. of 16)	0.008	(16)
Troilites (avg. of 7)	0.001	(16)
Stony meteorites	0.0008	(16)
Iron meteorites (avg. of 5)	0.6 ± 0.2[1]	(5)
Iron meteorite (one)	~ 2	(9)

[1] Determinations ranged from 0.335 to 1.95 ppm.

RHENIUM IN MOLYBDENITES

Of the many minerals analyzed by the Noddacks, molybdenite had by far the highest content of rhenium and many analyses have since been published. The data are widely scattered; some analyses have appeared in papers dealing with the radioactivity of rhenium and some in papers dealing with the search for technetium. It has therefore seemed worthwhile to assemble these analyses in Table 2, in which the arrangement is by the country of origin. The accuracy of some of the older analyses may be questionable.

Data on some of these deposits are given by Vanderwilt (24) and Creasey (6). No generalizations are evident as to the rhenium content and the type of geological occurrence. For example, the rhenium contents of molybdenites from porphyry copper deposits range from the low figures (0–50 ppm) at Bagdad, Copper Creek, and Copper Hill, Arizona; Chino, New Mexico; and Bingham, Utah; to the 100–150 ppm range of Cananea, Mexico, and Kounrad, U.S.S.R., the 150–688 ppm of Miami, Arizona, to the single determination of 1,030 ppm at the Nevada Consolidated mine. It is also evident that there is wide variation in samples from a single deposit. Unfortunately, with the

[2] The reference is not identified, but a recent paper (22) cites a thesis by S. M. Basitova (1950) on the geochemistry of rhenium.

TABLE 2

RHENIUM CONTENT OF MOLYBDENITES

(Most samples were concentrates)

Source	Re, ppm	MoS_2 content Wt. %	Reference
1. "U. S. A."	140	83.8	(8)
2. Arizona, Bagdad	20	—	(13)
3. Arizona, Copper Hill mine, Yavapai County	30	—	(13)
4. Arizona, Copper Creek	40	—	(11)
5. Arizona, Copper Creek	27.5	—	(11)
6. Arizona, Copper Creek	0	—	(11)
7. Arizona, Copper Creek[1]	20	—	(13)
8. Arizona, Miami, Gila County	152	—	(4)
9. Arizona, Miami, Gila County	150	—	(4)
10. Arizona, Miami, Gila County	297	—	(4)
11. Arizona, Miami, Gila County	688	—	(4)
12. Not stated[2]	70	—	(11)
13. Not stated[2]	325	—	(11)
14. Not stated[2]	597	—	(11)
15. "Colorado"	1.8	—	(16)
16. Colorado, Climax	5	—	(11)
17. Colorado, Climax	1.2	—	(11)
18. Colorado, Climax	28	82.5	(8)
19. Colorado, Climax	20	—	(4)
20. New Mexico, Chino mine	17.5	—	(11)
21. New Mexico, Questa	7.5	—	(11)
22. New Mexico, Questa	7.5	—	(11)
23. New Mexico, Questa	7.5	—	(11)
24. New Mexico, Questa	9	—	(11)
25. New Mexico, Questa	12.5	—	(11)
26. Nevada, McGill[3]	1030	—	(4)
27. Utah, Bingham	31	—	(11)
28. Utah, Bingham	44	—	(11)
29. Utah, Garfield	none	—	(11)
30. Utah, Garfield	none	—	(11)
31. Utah, Garfield	3.5	—	(11)
32. Utah, Garfield	6	—	(11)
33. Utah, Garfield	7	—	(11)
34. Utah, Garfield	37	—	(11)
35. "Canada"	20.4	99.6	(8)
36. Mexico, Cananea	120	92.1	(8)
37. "Brazil"	12.5	—	(11)
38. "Bolivia"	0.05	—	(16)
39. Chile, San Antonio	519	—	(10)
40. "Peru"	36	73.2	(8)
41. "Finland"	18	83.0	(8)
42. Sweden, Lainejaur	2500	—	(2)
43. "Norway"	8	91.9	(8)
44. Norway, Arendal	1400	98.6	(5)
45. Norway, Bandkeli	1.2	—	(17)
46. Norway, Drammon	7.5	—	(17)
47. Norway, Flekkefjord	12.1	97.2	(8)
48. Norway, Flekkefjord	5.0	—	(11)
49. Norway, Flekkefjord, Knaben mine	13.3	94.6	(8)
50. Norway, Flekkefjord, Knaben mine	1.4	—	(17)
51. Norway, Hvaleroyene	90	98.7	(8)
52. Norway, Lir	2	—	(17)
53. Norway, Lofoten	509	—	(10)
54. Norway, Moos	0.6	—	(17)
55. Norway, Nummedalen	811	—	(10)

TABLE 2—*Continued*

Source	Re, ppm	MoS_2 content Wt. %	Reference
56. Norway, Stavanger (avg. of 2)	3035	98.2	(8)
57. Norway, Stavanger (avg. of 2)	3130	—	(10)
58. Unknown, perhaps Stavanger	3250	98.5	(8)
59. Unknown, perhaps Stavanger	3040	98.0	(8)
60. Norway, Telemark	21	—	(16)
61. Germany, Mansfeld shale	~100	—	(9)
62. "Altenburg"	44	82.2	(8)
63. "Mine di Gonnesfadiga"	19.8	92.8	(8)
64. "Bulgaria"	5	46.5	(8)
65. Turkey, Keskin	50	98.4	(8)
66. U.S.S.R., "Siberia"	0.6	—	(16)
67. U.S.S.R., Kazakhstan, Chikoi	1.2	70.3	(3)
68. U.S.S.R., Kazakhstan, Kounrad (19[illegible])	150	—	(3)
69. U.S.S.R., Kazakhstan, Kounrad (1943)	100	20.1	(3)
70. U.S.S.R., Kazakhstan, Kounrad (1944)	100	16.9	(3)
71. U.S.S.R., Kazakhstan, Kounrad (1945)	150	82.1	(3)
72. U.S.S.R., Kazakhstan, Tyrny-Auz	10	—	(3)
73. U.S.S.R., Kazakhstan, Tyrny-Auz	2	—	(3)
74. U.S.S.R., Kazakhstan, Tyrny-Auz[4]	0–8	—	(22)
75. U.S.S.R., Umal'ta	5	—	(3)
76. "Japan"	10	—	(16)
77. Japan, Shirakawa	9.6	98.2	(8)
78. "Australia"	110	—	(15)
79. Australia, New South Wales	2.5	—	(17)
80. Australia, New South Wales, Kingsgate	48	—	(10)
81. German East Africa[5]	2710	98.2	(8)
82. Unknown	17.8	96.4	(8)

[1] Locality given as Childs-Aldwinkle mine.
[2] Placed here in the table because it seems a reasonable guess that these came from Miami.
[3] A smelter is located at McGill. Sample presumably from Nevada Con. mine, near Ely, Nevada.
[4] Analyses of 69 samples given. See Table 3.
[5] Stated elsewhere in same reference to be South West Africa.

exception of the samples from the Tyrny-Auz deposit, there are no geological data on the samples, most of which are concentrates.

The only study of the variation of rhenium content as related to geological occurrence is that of Studenikova and Zolotareva (22), who analyzed 69 molybdenites from the Tyrny-Auz deposit. Their results are summarized in Table 3. The range of rhenium content is rather small, with one exception, and the deposit is of an unusual type, so that the results are not very indicative.

Similar studies of samples collected with good geological control from such deposits as Miami would be very desirable. It would also be of great interest to have determinations of rhenium in samples of the amorphous form of MoS_2, jordisite.

References on the recovery of rhenium from molybdenite smelters are given by Sims et al. (21). Rhenium volatilizes as oxide during the roasting of the molybdenite and is enriched in the flue dusts. Bibikova (3) gives analyses of various flue dusts obtained by roasting ore containing 100 ppm Re; these contained 12, 30, 150, 360, and 2,000 ppm Re, and Cottrell dusts

TABLE 3

RHENIUM IN MOLYBDENITES OF TYRNY-AUZ (FROM (22))

Type of occurrence	No. of samples	Re content, ppm	
		Range	Average
1. Skarns	13	0.13–8.0	3.8
2. Leucocratic granite	6	0–0.1	0.1
3. Quartz veinlets in biotite hornfels	7	2–5	3.4
4. Quartz veinlet in leucocratic granite	1	1.8	1.8
5. Quartz veinlets in skarn	7	0–8	2.7
6. Quartz-feldspar veinlets in biotite hornfels	6	1–3.5	2.2
7. Skarn veinlets	10	0–7	3.7
8. Quartz-garnet veinlets in leucocratic granites	8	0–6	2.5
9. Quartz-garnet veinlets in skarns	10	0–8	4.9
10. Veinlets in El'dzhurtinsk granites	1	140	140

contained 900 ppm Re. Boyd and Larson (4) reported 3,130 ppm Re in a flue dust from Miami and stated that other samples contained up to 2 percent Re.

RHENIUM IN MOLYBDATE MINERALS

One might reasonably expect that rhenium would be present in appreciable amounts in molybdate minerals; the ionic radii of sexivalent rhenium must be close to that of sexivalent molybdenum and the ionization potentials of Mo^{+6} and Re^{+7} are also close. The available analyses, collected in Table 4, show that this is not the case.

It is an intriguing problem as to whether molybdenum and rhenium separate during their oxidation from the quadrivalent state. There has been considerable uncertainty as to the origin of wulfenite in ore deposits. At present the prevailing belief is that it was formed by reaction of lead in the ore deposit with molybdenum leached from overlying sediments, especially shales. (See Schroll (19), Meixner (14), and many references cited by them.) If this is correct, the molybdenum and rhenium of wulfenite are not

TABLE 4

RHENIUM IN MOLYBDATE MINERALS

Locality	Re, ppm	$PbMoO_4$, %	Reference
1. Wulfenite, Mammoth mine, Arizona	0.12	49.7	(8)
2. Wulfenite, Red Cloud mine, Arizona	0.38	78.4	(8)
3. Wulfenite, Bennett mine, N. Mex.	0.37	71.5	(8)
4. Wulfenite, Zacatecas, Mexico	0.05	7.7	(8)
5. Wulfenite, Atacama, Chile	0.06	16.8	(8)
6. Wulfenite, Bleiberg, Austria	0	—	(16)
7. Wulfenite, Bleiberg, Austria	0.88	47.8	(8)
8. Wulfenite, Bleiberg, Austria	0.62	58.5	(8)
9. Wulfenite, Partenkirchen	0.25	7.7	(8)
10. Wulfenite, Garmisch	1.25	56.6	(8)
11. Molybdenum ocher, Knaben, Norway	0	—	(16)

derived directly from oxidation of molybdenite. It would be of great interest to have determinations of the Mo/Re ratio in bituminous shales; none has yet been made.

Relative solubilities of molybdenum and rhenium compounds may play an important role in this apparent separation. The recent report by Petersen, Hamilton, and Myers (18) of rhenium contents up to 0.1 percent in Triassic sedimentary rocks from Coconino County, Arizona, is of particular interest, because they report it to be associated with molybdenum and uranium, and because they found that the rhenium was, at least in part, in a water-soluble form (Re_2O_7?).

RHENIUM IN OTHER MINERALS

No mineral other than molybdenite or wulfenite (analyses calculated to pure mineral) has been found to contain as much as 2 ppm Re. Below are listed some of the minerals in which as much as 0.01 ppm Re has been reported.

The Noddacks (16) reported 0.02 ppm in a scheelite and the same amount in a wolframite. The very rare mineral tungstenite, WS_2, reported from only two localities in the world, seemed to be a likely host mineral for rhenium, but a spectrographic analysis made by Harry Bastron of the U. S. Geological Survey showed no rhenium in a sample from the type locality, Emma mine, Utah. However, the sensitivity of the analysis was low, perhaps 50–100 ppm Re.

The Noddacks reported no rhenium in the few manganese minerals they studied, a somewhat surprising result in view of the relationship in the Periodic Table. Hurd and Hiskey (12) analyzed 80 samples of "pyrolusite" from many localities and found 0.1 ppm Re in 7 samples, 0.2 ppm in one sample. One might predict with some confidence that rhenium is likely to be present in small amounts in the flue dusts of smelters that roast manganese oxides or carbonates.

The Noddacks (16) found 0–1 ppm Re in 5 samples of platinum group minerals and ores, but Boyd and Larson (4) found none in an osmiridium concentrate from South Africa. The Noddacks also reported 0.01–0.08 ppm Re in about 15 different sulfides, including chalcopyrite, argentite, and marcasite. The selenides clausthalite (PbSe) and berzelianite (Cu_2Se) were especially high in rhenium (0.8 ppm, 0.2 ppm). They also found 0.01–0.02 ppm Re in cassiterite, rutile, and chromite.

The Noddacks (16) also found concentrations of rhenium in some pegmatite minerals, notably in the alvite variety of zircon (up to 0.6 ppm Re), gadolinite (up to 1.1 ppm Re), thortveitite (0.6 ppm Re), columbite-tantalite (0.03–0.2 ppm Re), and in complex tantalate-niobates (fergusonite, euxenite, samarskite) (0.01–0.02 ppm Re). Sen (20) recently found 0.26 ppm Re in a columbite. Boyd and Larson (4) found no rhenium in a sample of yttrotantalite.

These fragmentary results indicate that rhenium concentrates somewhat in hydrothermal ore-forming solutions and in late-stage pegmatitic solutions.

POSSIBLE FUTURE SOURCES OF RHENIUM

The total production of the world was guessed in 1956 (21, p. 166) to be of the order of magnitude of 1,000 to 2,000 pounds of metal per year, all derived from the smelting of molybdenite. This was estimated to be a small fraction, perhaps 5–10 percent, of the potential production. Obviously the first step in increasing production is to install recovery processes in existing molybdenite smelters. It is possible also that present recoveries could be improved.

The work of the Noddacks does not suggest any other potential source. Perhaps even more discouraging is the fact that the spectrographic analyses published by Kaiser et al. (13) of nearly 1,000 samples of smelter products showed rhenium only in molybdenites. These analyses were, however, of comparatively low sensitivity (perhaps 20–50 ppm Re) and it is quite possible that a good source has been overlooked. It should not be forgotten that the maximum content in molybdenite in Table 2 is 150 times that reported by the Noddacks. Systematic analyses of the flue dusts collected in smelters using oxidizing roasts of sulfide minerals may well turn up a source of rhenium not now guessed.

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STRUCTURE AND ROCK ALTERATION AT THE ELIZABETH MINE, VERMONT

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PART II

ROCK ALTERATION AT THE ELIZABETH MINE

ABSTRACT

The Elizabeth mine orebodies are concordant within the Gile Mountain formation at the contact of amphibolite and mica schist. The ore consists of massive and disseminated sulfides comprised principally of pyrrhotite and chalcopyrite. The wallrocks of the orebodies show considerable metasomatic reaction involving the addition of potassium, copper, sulfur, and water, and the removal of sodium, calcium, magnesium, carbonaceous matter and CO_2. The principal mineralogic changes that take place farthest from the ore are the pseudomorphic replacements of kyanite by muscovite, hornblende and garnet by biotite, calcite, pyrrhotite, and minor quartz, and the disappearance of carbonaceous matter within schist. Adjacent to the ore all silicate minerals including plagioclase are replaced by sericite.

Apart from the above-mentioned alteration and later regional retrograde metamorphic effects, two other types of alteration are present within the mine; one predating, and the other postdating the alteration associated with the ore. It is believed that all three types of alteration were formed as a continuous process during decreasing temperature conditions following the thermal peak of metamorphism. Channelling of solutions from their initial passageways along permeable zones within amphibolite to more permeable zones associated with structural features led to the metamorphism of the earlier alteration zones and resulted in the formation of the metamorphic index minerals, garnet and staurolite within altered amphibolite.

The various assemblages of ferromagnesian minerals suggest that alteration commenced shortly after the thermal peak of metamorphism and persisted through staurolite and garnet and possibly to chlorite grade of metamorphism during decreasing temperature. Although some weak mineralization is associated with the earliest and latest alteration, mineralization in the form of ore only accompanies alteration corresponding to metamorphic temperature and pressure intermediate between these two extremes.

INTRODUCTION

Apart from the minor effects of post-Acadian regional retrograde metamorphism, three types of alteration are present within the Elizabeth mine. Of these only one, stage 2 alteration, is associated with the orebodies. The general relationships of all three types to the various metamorphic rocks and their structure indicate that they were formed during the Acadian orogeny (middle or late Devonian).

Chemical and mineralogical changes involved in the alteration of rocks are much more profound in amphibolite than in mica schists, and for this reason descriptive data presented are largely from alteration zones within amphibolite. Particular emphasis is placed on the study of stage 2 alteration associated with the orebodies.

SULFIDES

Pyrrhotite is the principal mineral in the Elizabeth mine copper orebodies. Other minerals, listed in order of abundance, are chalcopyrite, sphalerite, cubanite, pyrite, and rare valleriite, galena, tetrahedrite, and tennantite. Molybdenite is present in minute amounts.

The mineralogy of the sulfides has been adequately discussed by McKinstry and Mikkola (8), and Buerger (1, p. 437) and will not be discussed in this paper.

The ore occurs as massive sulfide bands, disseminated sulfides in schist and less commonly as coarse-grained aggregates filling narrow cross-cutting fractures in the wallrock. The sulfides have a maximum grain size in the fractures where pyrrhotite and chalcopyrite grains reach diameters of 20 mm. Sporadic grains of sphalerite may be as large as 5 mm in diameter. In the massive sulfide bands, the grain size varies from 0.1 to 0.5 mm in diameter. Pyrite is generally present as small ragged grains less than 0.1 mm in diameter, although cubes as large as 50 mm in size have been noted. The grain size of the disseminated sulfide ore ranges from 0.05 to 0.5 mm in diameter.

Within the ore zones, gangue minerals consist of quartz, plagioclase, calcite, biotite, actinolite, sericite, idocrase sphene, apatite, tourmaline, and rutile. Of these minerals, plagioclase, biotite, sericite, and actinolite are remnants of unreplaced rock within the ore. Both tourmaline and rutile are present in the ore zone as euhedral crystals embedded in coarse-grained segregations of pyrrhotite and chalcopyrite which fill gash veins.

From the general appearance of the ore and from millhead assays, it is clear that pyrrhotite and chalcopyrite exhibit a zonal relationship within the Elizabeth mine. The weighted average assay of several hundred feet of ore from diamond drill holes indicates a grade of 32.1% Fe and 1.1% Cu for massive ore in the southern section of the deposit and 21.4% Fe and 4.9% Cu for massive ore in the northern section of the deposit. Thus the Cu : Fe ratio changes from 1 : 29 in the south to 1 : 4 in the north. The average assays of Fe and Cu cited, together with results of semi-quantitative analyses [1] of bulk samples made from the above diamond drill hole cores are tabulated below. The elements listed in each column are arranged in decreasing order of abundance. Comparison of the relative strength of the lines of the various elements however indicates that the southern end of the mine is richer in Fe, Mn, Ti, Zr, Mo, Co, Ni, and Au compared to the northern section of the mine, whereas the northern section of the mine is richer in Cu, Zn, Pb, and Ag than the southern section.

[1] By J. Ito, Department of Mineralogy and Petrography, Harvard University.

Element	Southern section of mine (8900N to 10200N) Weight, %	Northern section of mine (14250N to 15250N) Weight, %
Fe	32.1	21.4
Cu	1.1	4.9
Mn	>1	>1
Zn	0.1 to 1	0.1 to 1
Pb		
Ti		
Zr	0.001 to 0.1	0.001 to 0.1
Mo		
Co		
Ni		
Ag		
Au	<0.001	<0.001
In		
Cb		

In general, this change in composition of the ore is gradual from one end of the mine to the other and corresponds to a progressive change in the mineralogy of the altered wallrock.

WALLROCK

The Elizabeth mine orebodies are bedded within the Gile Mountain formation, and are bounded on their footwall side by amphibolite, and on their hangingwall side by quartz-mica schists and quartzites. These rocks have been described, and estimated modes of the common types presented (Table 1) in Part I [2] of this paper.

MINERALOGY OF METAMORPHIC MINERALS OF THE WALLROCKS

Mineralogical data are presented below to record the compositional ranges of metamorphic minerals involved in the reaction between the ore solution and wallrock. Study was confined to the major rock-forming minerals, namely, plagioclase, hornblende, biotite, and garnet.

Plagioclase.—The An content of plagioclase was determined by indices of refraction and X-ray methods. Indices were determined chiefly to confirm the composition determined by the X-ray methods described by Goodyear and Duffin (4, pp. 319–324), Chayes and Robbins (2, pp. 46–49), and Tuttle and Bowen (12, p. 594).

The range in composition in terms of anorthite component varies from 5 to 38 mol. percent. The lowest (An_5) and highest (An_{38}) anorthite content determined were from a zoned euhedral crystal within a metamorphic pegmatite. The range of composition of plagioclase within amphibolite is An_{17-32}. The range of composition of plagioclase within schists and quartzites is An_{15-36}.

Amphiboles.—As amphiboles contain many components the determination of the true composition without chemical analysis is difficult. Foslie (3,

[2] Structure of the Elizabeth Mine. Previous issue.

p. 78) has published the curves for analyzed amphiboles of the epidote-amphibolite facies in which the mean index of refraction $\alpha + \beta + \gamma/3$ is plotted against their *mg*-number (after Niggli) defined as:

$$mg = \text{mol.} \frac{\text{MgO}}{2\text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO} + \text{MgO}}.$$

Once the nature of the amphibolite (tremolite-actinolite or hornblende) was determined by microscopic study, the mean refractive indices of 15 hornblendes were applied to the appropriate Foslie curve. The *mg*-numbers so obtained ranged between 34 and 61. Application of the same indices to the curves of Tröger (11, p. 77) gave *mg*-numbers ranging from 28 to 55, and in the case of each mineral studied, the *mg*-number as determined from graphs of Tröger was 6 ± 1 less than the corresponding value from the Foslie curve. As the curves of Foslie appear valid for analyzed hornblendes from the Littleton quadrangle (Billings, 1937, p. 556) and the hornblendes at the Elizabeth mine are in epidote-amphibolite, the determinations by the Foslie method are preferred to those of Tröger.

The hornblendes from the Footwall-Hangingwall amphibolite show very little range in *mg*-number (51–53). The number of specimens studied (4) is too few on which to base any definite conclusions; however, it is noteworthy that this bed shows very little variation in texture or proportion of the mineral assemblages. On the other hand, the variation of *mg*-number (34–61) of the Westwall amphibolite is coincident with considerable variation in texture and relative proportion of the contained minerals. Compositional variation in the bed is quite apparent, and it is assumed that variation in *mg*-number of the hornblende reflects such changes.

Biotite.—Next to quartz and muscovite, biotite is the commonest mineral in the metamorphic rocks of the area. The β index of refraction of biotite ranges from 1.590 to 1.658. The lowest β index determinations are from the lime silicate rocks found adjacent to the ore zone, while the highest are from some amphibolites. The schists and quartzites have indices that are intermediate between the two extremes.

Garnet.—Almandine is a common mineral in the area and varies in size from microscopic to approximately 70 mm in diameter. The largest and most densely distributed almandines are found in alteration zones within amphibolite beds. They are also present although much less common in unaltered amphibolite, and rarely exceed diameters of 9 mm. Relatively small garnets (averaging 2 to 4 mm in diameter) are widely developed throughout the Gile Mountain formation schists in the vicinity of the mine.

The writer believes that two generations of almandine exist within the mine. The first developed during progressive metamorphism of the sediments in the area. Those of the second generation are confined to alteration zones and are believed to post-date alteration.

The refractive index of fifteen garnets from various rocks in the mine showed a surprisingly small range of variation: .009 between 1.798 and 1.807. Those from the Gile Mountain formation schist fell in the lower range (1.798–1.803) of the overall number determined, but overlapped with the

refractive index of second generation garnets in stages 1 and 2 alteration zones. A chemical analysis of a garnet was made from garnet-sericite schist from the alteration zone immediately adjacent to ore in Pit No. 2. The schist contained garnet, chromium sericite,[3] quartz, disseminated sulfides, and minor amounts of oligoclase, pale biotite, calcite, and rutile. The chemical analysis of the garnet, its formula, optical and physical data are given in Table 1.

The slight variations in both refractive index and length of the unit cell edge (A_o) suggest that the compositions of the garnets studied do not differ

TABLE 1

CHEMICAL ANALYSIS OF GARNET FROM GARNET-MUSCOVITE SCHIST (EZ 329) WITHIN THE WESTWALL AMPHIBOLITE

Coordinate position, 9500N, Pit No. 2, Elizabeth mine, Vermont.
Analyst—J. Ito, Harvard University.

	Weight, %
SiO_2	36.09
Al_2O_3	20.36
Fe_2O_3	0.38
FeO	31.90
MnO	1.18
CaO	7.38
TiO_2	—
Cr_2O_3	Tr
Na_2O	—
K_2O	—
H_2O	Not determined
	99.72

Structural formula of garnet:

$$(Fe_{2.18}\,Mg_{.14}\,Mn_{.17}\,Ca_{.66})\ (Fe_{.02}\,Al_{1.96}\,Si_{2.98}\,O_{12})$$

Molecular proportions of garnet components:

	Percent
Almandine	69
Grossularite	21
Spessartite	6
Pyrope	4
Andradite	1

Refractive index: 1.805
Specific gravity: 4.01
Length of unit cell edge (A_o): 11.59

appreciably. To a certain extent, this is probably due to a too limited study, because in some cases, the second generation garnets in the alteration zones are appreciably lighter in color than the first generation garnets.

TYPES OF ALTERATION

Rock alteration in the Elizabeth mine may be divided into four types which are distinguished from each other on the basis of mineralogy and distribution. These types of alteration have been designated stages 1, 2, 3, and 4, in the belief that they can be arranged in chronological order. Stage

[3] See Table 5 for chemical analysis.

4 represents the minor retrograde metamorphic effects present throughout the region. The first three stages are believed to represent a continuous period of alteration during the decreasing temperature conditions of metamorphism. The subdivision into three stages is therefore arbitrary in that they are actually gradational into each other. The use of the word "stage" is introduced to clarify the discussion on the differences between early, middle, and later alteration phenomena.

The alteration envelopes of stages 1 and 2 may be divided into two subzones, on the basis of mineralogic differences: (1) an outer *biotite subzone*, and (2) an inner *sericite subzone*. Broadly the biotite subzone is characterized by the pseudomorphic replacement of hornblende and garnet by biotite, kyanite by muscovite, removal of carbonaceous matter from mica schists, and the stability of plagioclase and carbonate. The sericite subzone is characterized by the pseudomorphic replacement of plagioclase and biotite by sericite and the removal of carbonate.

The alteration envelope of stage 3 may be divided into an outer *chlorite subzone* and an inner *sericite subzone*. Broadly the chlorite subzone is characterized by the pseudomorphic replacement of hornblende, garnet, and dark biotite by chlorite, kyanite by muscovite, removal of carbonaceous matter from mica schists and the stability of plagioclase and carbonate. The sericite subzone is characterized by the pseudomorphic replacement of chlorite and plagioclase by sericite and the removal of carbonate.

The subdivision into two clear-cut subzones is not always valid in stage 1 alteration, where the two zones overlap with the result that a narrow sericite subzone and a narrow biotite subzone are separated by a wide intervening zone having some of the characteristics of each. For instance, in amphibolite, biotite is developed after hornblende, and sericite is developed at the expense of plagioclase though not necessarily after the biotite, as is the case in the sericite subzone. In several localities, the superimposed sericite and biotite subzones extend to the limit of alteration without the existence of a separate biotite subzone in the sense defined above.

In addition to these broad mineralogic characteristics, post-alteration garnets may be present in the biotite subzone or in the superimposed biotite-sericite subzone within the Gile Mountain formation schists or amphibolites. Likewise staurolite may be present in the biotite subzone within amphibolites.

DISTRIBUTION AND SIZE OF THE ALTERATION ZONES

The distribution of stages 1, 2, and 3 alteration zones are described below and illustrated in Figure 1.

Stage 1 Alteration.—Alteration of this type is evident as lenticular zones parallel to bedding within amphibolites and to a lesser extent within schists. The lenses are as much as sixty feet wide and several hundred feet long in both longitudinal and dip length. They are unrelated to faults, shears, or shear zones and are randomly distributed in relation to fold structures. Where alteration is present in anticlinal and synclinal positions, the alteration lenses wrap about the folds in conformity with the attitude of bedding.

Stage 1 alteration is the same or similar to zones present in the Standing Pond amphibolite and associated amphibolites of the Gile Mountain formation throughout Vermont. Whether accessory pyrrhotite or chalcopyrite are present in all or some of the zones away from the vicinity of the Elizabeth mine is not known.

Stage 2 Alteration.—This type of alteration is associated with the Elizabeth orebodies. The overall width of the alteration envelope varies considerably from point to point through the mine. In the schists adjacent to the orebodies, the width varies from a few inches to a maximum of 20 feet and averages 6 feet in the northern section of the mine, and less than one foot through much of the southern section of the mine. In amphibolite, the width of alteration is noticeably narrower than in the schists and has a maximum width of nine

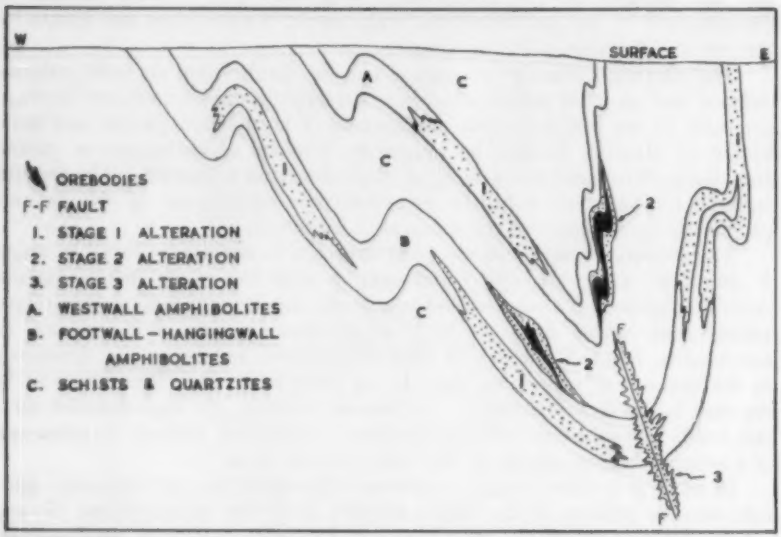


FIG. 1. Diagrammatic cross-section showing the distribution of alteration zones.

feet while averaging approximately two feet in the northern section, and less than one foot in the southern section of the mine. In the latitudes of 9000 to 11000N, the width in places is as little as one inch.

Because the orebodies lie parallel to bedding, alteration has advanced away from the ore to a specific bed only in those places where the width of alteration is constant, and there is no variation in the width of the stratigraphic units involved. In general, there is considerable fluctuation in the width of alteration from point to point, and as a result, the alteration envelope transgresses bedding to varying degrees as illustrated in Figures 2 and 3. Where the ore is tabular in shape and varies from a few inches to ten feet in thickness, a reasonable correlation exists between ore thickness and the width of

alteration in a given section of the mine. However, where the ore is thick (15 to 40 feet) in fold positions, there is generally a poor correlation between the width of ore and the width of alteration. This is thought to have been due to varying degrees of rock flexure with resultant changes in permeability during the introduction of the ore solutions.

Alteration that is mineralogically identical to the alteration adjacent to the main ore zone accompanies cross-cutting fractures that transect the wallrock and extend beyond the limits of the main envelope of alteration (Fig. 2a). Such fractures are filled with sulfides and range in width from a millimeter to

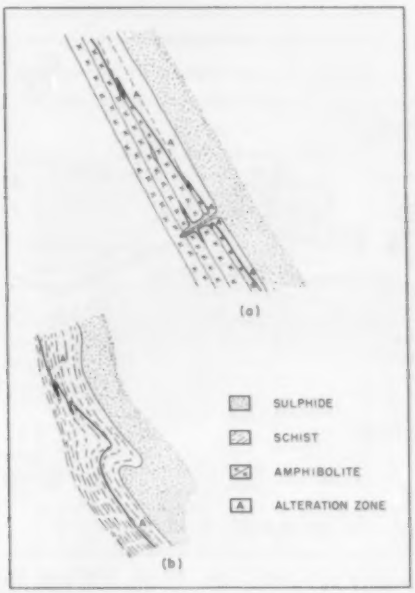


FIG. 2. Diagrammatic cross-sections showing the shape of alteration zones in relation to ore and bedding planes in (a) amphibolite and (b) schist.

several inches, while the corresponding width of alteration varies from one-half to three inches.

Stage 3 Alteration.—Alteration of this type is found in well-defined zones, above and below, to the east and west of the ore zones within a known distance of approximately 500 feet.

The zones are structurally controlled by folds (?), post-ore faults, shears, and shear zones, and are generally less than thirty feet in width. As the mine workings rarely intersect this type of alteration, and information is largely based on drill holes, little is known of the length and height of individual zones.

SIGNIFICANCE OF PERMEABILITY IN ROCK ALTERATION

In the study of alteration of amphibolite, it is noticed that thin sheaths of alteration parallel to bedding occur as much as one foot beyond the limits of the alteration envelope. Such alteration is generally confined to bands one-quarter to one-half inch wide within amphibolites that are high in plagioclase content. In some cases, these layered alteration sheaths are connected to cross-cutting fractures or to the main alteration envelope, as illustrated in Figure 2a. Isolated alteration sheaths are common in the schists and occur as much as twenty feet farther out than the outer edge of the alteration envelope.

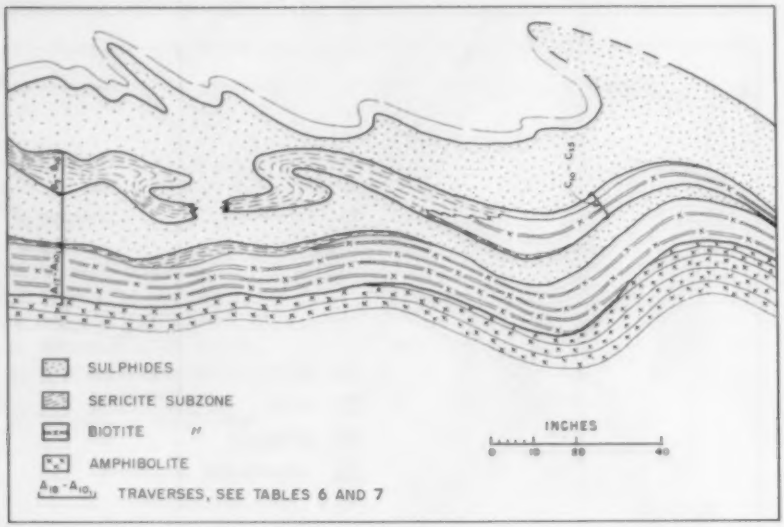


FIG. 3. Cross-section at 14200N, No. 3 drift, 975 level looking north, showing the encroachment of the alteration zone across amphibolite and its gneissosity. Band marked B_9–B_{18} and C_{10}–C_{18} passes from sericite subzone of alteration at the left hand end of the diagram through biotite subzone of alteration at the right hand end and finally into amphibolite farther to the right. A_{10}–A_{10}, B_9–B_{18}, and C_{10}–C_{18} are positions from which specimens were collected for study. Data are presented in Tables 6 and 7.

The macroscopic appearance of the various bands within amphibolite suggests that permeability is greater in the plagioclase-rich bands, which are selectively altered. The author undertook a laboratory examination to determine if these impressions could be substantiated by experimental data.

Over fifty determinations of permeability were made on altered and unaltered wallrock specimens from within the Elizabeth mine. A number of values are tabulated on Table 2. The equipment and procedure used in determining permeability were those used by Ohle (9).

Too few samples were studied to determine the range of permeability in specific rock types. However, of those studied, unaltered schists showed permeabilities lower than any other rock type, and specimens from the sericite subzone of alteration showed the highest permeabilities. The study gave a quantitative estimate of the variation in permeability along schistosity compared to the permeability across the structure. In Table 2, the difference between individual pairs 1 and 2, 5, and 6, 12 and 13, and 19 and 20 averages approximately fivefold.

In regard to amphibolite, the study indicated that (1) the banded amphibolites have permeabilities greater than unaltered schists or quartzites;

TABLE 2

PERMEABILITIES[1] OF ALTERED AND UNALTERED WALL ROCK FROM THE ELIZABETH MINE

	Specimen number		Rock type	Relation to schistosity	Permeability (millidarcies)
1	EZ 221	Unaltered amphibolites	FG[2] banded amphibolite	across	270 × 10^{-6}
2	EZ 221		FG[2] banded amphibolite	along	1,600 × 10^{-6}
3	EZ A18		Uniform grained amphibolite	across	11 × 10^{-6}
4	EZ A22		Dark band of amphibolite	across	160 × 10^{-6}
5	EZ A20		Light band of amphibolite	across	400 × 10^{-6}
6	EZ A20		Light band of amphibolite	along	1,600 × 10^{-6}
7	EZ E	Altered amphibolites	Biotite subzone (stage 2)	across	140 × 10^{-6}
8	EZ D		Biotite subzone (stage 2)	across	1,800 × 10^{-6}
9	EZ A13		Biotite subzone (stage 2)	across	95 × 10^{-6}
10	EZ A11		Biotite subzone (stage 2)	across	100 × 10^{-6}
11	EZ B10		Sericite subzone (stage 2)	across	950 × 10^{-6}
12	EZ B56		Sericite subzone (stage 1)	across	660 × 10^{-6}
13	EZ B56		Sericite subzone (stage 1)	along	4,300 × 10^{-6}
14	EZ B56		Sericite subzone (stage 1)	along	7,500 × 10^{-6}
15	EZ 267	Unaltered sch. and qtz.	Quartzite	—	25 × 10^{-6}
16	EZ 268		Quartzite	—	39 × 10^{-6}
17	EZ 218		Dark[3] muscovite schist	across	8 × 10^{-6}
18	EZ 277		Dark[3] muscovite schist	across	9.4 × 10^{-6}
19	EZ 370	Altered schist	Sericite subzone (stage 2)	across	1,000 × 10^{-6}
20	EZ 370		Sericite subzone (stage 2)	along	2,300 × 10^{-6}
21	EZ 264		Sericite subzone (stage 2)	across	10,000 × 10^{-6}

[1] Permeabilities determined using nitrogen gas.
[2] FG denotes fine grained.
[3] Color due to carbonaceous material.

(2) permeability in the light plagioclase bands is greater than in bands containing a substantial amount of hornblende and calcite; (3) permeability is greater along gneissosity than across it, evidently because of preferential flow along the plagioclase-rich bands; (4) permeability is much greater along than across the bedding of fine-grained amphibolite due to preferred orientation of hornblende in the plane of bedding; and (5) altered amphibolite is more permeable in the sericite subzone than in unaltered amphibolite.

It is realized that these permeabilities do not represent the permeabilities in the rocks at the time of alteration. Significantly higher pressures associated with metamorphic conditions would effectively decrease the perme-

abilities of the various rocks. However, the relative differences existing between the determinations presented should be meaningful.

LABORATORY PROCEDURE

The study of alteration involved the detailed study of one sectional traverse from unaltered amphibolite through the alteration envelope to the ore zone. Chemical, X-ray, thin section, and polished section studies were carried out together with determination of the specific gravity, porosity, and permeability. X-ray, thin section, and matching polished section study were carried out on a second traverse, and three additional traverses were studied without the aid of polished sections. Apart from these five traverses, thin section and X-ray studies were made on specimens of special interest from various points throughout the mine. Where the relationship between opaque and silicate minerals could not be ascertained from matching thin and polished sections, polished thin sections were studied.

The five traverses referred to above consisted of adjoining blocks of rock that extended from the orebody through the alteration envelope into unaltered rock. Each block was cut into three parallel slabs $\frac{1}{4}$ to $\frac{1}{3}$ inch thick. Each parallel series of slabs, adjoining end-to-end across the alteration envelope, was cut into small blocks measuring approximately $1\frac{1}{4} \times \frac{3}{4} \times \frac{1}{3}$ of an inch. A continuous set of adjoining thin sections and random polished sections were made of one series of blocks, specific gravity and porosity determinations from another, and partial chemical analyses [4] and X-ray studies from the third series. The parallel series of blocks were separated from each other only by the width of the blade of a diamond-edged saw.

From the partial chemical analyses, the values of various components expressed in weight percent were plotted on a cross-section normal to the orebody at a scale of 1 inch equals 10 inches, so that each component of each block was represented as a single point. By this method, the value of a component at any point within the alteration zone could be compared to the value of that component in the unaltered rock and to other components at that point. Only those components that appeared to be the most significant to the study were determined. These included K_2O, Na_2O, and total Fe and Cu. A limited number of determinations were made for CaO, MgO, Cr_2O_3, SiO_2, and S. Variations in CO_2, and H_2O content of the specimens could be estimated by thin-section study while FeO content in silicate minerals could be estimated by comparison with MgO content and the modal analysis from thin-sections.

A study of Tables 6 and 7 shows that discrepancies exist if any attempt is made to convert the value of a certain component into a modal percentage of a particular mineral in the rock: for instance, estimation of sericite that should be in the rock assuming all K_2O within the rock is contained in that mineral. Such errors reflect the inherent shortcomings of the sampling procedure, unavoidable due to the lack of homogeneity of the banded rocks over the

[4] Partial and complete chemical analyses were carried out by J. Ito, analyst for the Department of Mineralogy and Petrography, Harvard University.

short distances between adjacent samples. As alteration transgresses strike, care was taken to avoid studying rocks exhibiting macroscopically visible compositional variation across their strike. Macroscopically, the biotite subzone in amphibolite differs from the unaltered amphibolite only in the replacement of biotite after hornblende. Thus compositional variation of ferromagnesian content across the alteration zone could be recognized by the variations in amount of ferromagnesian minerals across a traverse as shown in modal analyses.

It is felt that despite any of the comparatively small discrepancies which may exist between chemical, modal, and porosity data in this study, the mineralogical and chemical changes across the altered wallrock are so great that the gross features may be interpreted without doubt as to their validity.

MINERALOGY OF THE ALTERATION ZONES

The broad mineralogic characteristics of the alteration zones are summarized in Table 3. Details are described below.

TABLE 3

CHARACTERISTICS OF THE ALTERATION ZONES

	Distribution	Metamorphic zone	Mineralogical subdivisions	Characteristic minerals
Stage 1 (pre-ore)	Permeable rocks	Staurolite to garnet	Biotite subzone	Black biotite after hornblende. Magnetite, minor pyrrhotite and chalcopyrite. Muscovite after kyanite.
			Sericite subzone	Sericite after all silicate minerals. Magnetite, minor pyrrhotite and chalcopyrite.
Stage 2 (ore stage)	Associated with structural features	Garnet to biotite	Biotite subzone	Pale biotite after hornblende and garnet. Muscovite after kyanite. Minor chlorite, pyrrhotite, chalcopyrite and rare sphalerite. No magnetite.
			Sericite subzone	Sericite after all silicate minerals. Abundant pyrrhotite, chalcopyrite and rare sphalerite.
Stage 3 (post-ore)	Associated with structural features	Chlorite	Chlorite subzone	Chlorite after all ferromagnesian minerals. Muscovite after kyanite. Minor pyrrhotite and chalcopyrite. No magnetite.
			Sericite subzone	Sericite after plagioclase and chlorite.
Stage 4	Regional	Chlorite	—	Minor chlorite rimming ferromagnesian minerals.

Stage 1 Alteration (Pre-ore)

The descriptive data presented below are those of alteration zones within amphibolite. Alteration of schists is similar, the end product of alteration being a silvery quartz-sericite schist.

Biotite Subzone.—The alteration effects involve the pseudomorphic replacement of hornblende by black biotite, calcite, magnetite, and a minor number of elongated blades of quartz. Accessory pyrrhotite is interspersed within the biotite pseudomorphs and where more plentiful may be seen at intergranular boundaries throughout the rock. Chalcopyrite is rare. Plagioclase, carbonate, and clinozoisite, where present, are stable. However, minute wisps of white mica are present at the intergranular boundaries of plagioclase grains and in places embay their frayed edges. X-ray examination of the white mica yields a muscovite diffraction pattern.

The Fe : Fe + Mg ratio of biotite after hornblende corresponds to the Fe : Fe + Mg ratio of the hornblende (Table 4). Fourteen specimens containing hornblende and/or biotite pseudomorphic after hornblende were collected from random points 1,000 feet along the strike of the Westwall amphibolite at Pit. No. 2. The Fe : Fe + Mg ratio of the hornblende and biotite were estimated by applying the refractive indices of the hornblende to the curve of Foslie (3), and the β index of the biotites to the graph of Winchell (13, p. 374). The alumina content of the biotites was assumed as annite-phlogopite 60 percent, siderophyllite-eastonite 40 percent.

Although almandine garnets are present in amphibolite in the vicinity of the mine, they are so uncommon that the writer has not observed an alteration zone developed across a garnet-bearing amphibolite. On the other hand, almandine garnets are not only everywhere present in the alteration zones themselves but are generally developed in profuse numbers. Where the edge of the alteration zone is gradational into fresh amphibolite, the garnets show a pronounced gradation in size normal to the bedding. The smallest garnets (2 to 5 mm in diameter) are at the outer edge of alteration where hornblende is rimmed by biotite. They become progressively larger toward the more altered phases of the zone and reach a maximum observed size of 70 mm in diameter. More commonly they range from 15 to 25 mm in diameter.

Other minerals present in the biotite subzone include staurolite, chlorite, sphene, and orthoclase. Staurolite is free from any alteration products and has a maximum grain size of 2 mm in diameter. Chlorite is a minor constituent and occurs as distinct laths within pseudomorphs after hornblende as well as laths interleaved with biotite. Orthoclase has been noted where appreciable replacement of plagioclase by sericite has occurred.

The common assemblage of ferromagnesian minerals is biotite-garnet-chlorite, and the relatively uncommon assemblages, biotite-garnet-staurolite, and biotite-staurolite.

Sericite Subzone.—At the most advanced stage of alteration, the mineralogy of the sericite subzone is simple, consisting of chromian, or white sericite, magnetite, minor quartz, rutile, apatite, pyrrhotite, and chalcopyrite.

However, this degree of alteration is rarely present, and rock generally contains, in addition to the above-mentioned minerals, minor biotite, calcite, clinozoisite, and sphene.

There is generally no sharp demarcation between the sericite and biotite subzones, and in the greater part of the alteration zones within amphibolite, sericite may replace 50 percent of the original plagioclase before appreciable pseudomorphic replacement of biotite by sericite is discernible. Sericite fills the frayed edges and embayments at the edges of plagioclase grains, and, in some cases, a single sericite plate envelops a small ragged remnant of plagioclase. No selective alteration along cleavage or twin planes is evident. Pseudomorphic replacement of biotite by sericite takes place along cleavage planes without the appearance of phlogopite as an intermediate phase as is the case in stage 2 alteration. Sericite after biotite is distinguished from sericite after plagioclase by the presence of poikilitically-included magnetite.

Where garnets occur in the superimposed sericite and biotite subzones, the garnets, as in the biotite subzone, are commonly surrounded by haloes free from any biotite. The haloes range up to twice the diameter of individual garnets, and in some cases are a conspicuous textural feature of the rocks. The haloes are commonly apple-green due to the presence of chromian sericite.

Stage 2 Alteration (Accompanying Ore)

Biotite Subzone.—The principal points that distinguish the biotite subzone of stage 2 from the biotite subzone of stage 1 are the presence of pale biotite in place of black biotite, the abundance of disseminated sulfide, absence of magnetite, and the comparatively rare occurrence of garnet.

As in stage 1, the alteration effects within amphibolite are quite simple and involve the replacement of hornblende by pale biotite, calcite, and the occasional appearance of narrow elongated grains of quartz. Iron released from the breakdown of hornblende is at least in part fixed as pyrrhotite. Magnetite is absent. Although the shape of original hornblende grains in places is perfectly preserved by the alteration products, it is more common to find that the products are dispersed over a volume two, three or more times the average grain size of individual hornblende grains. The alteration products therefore are segregations after hornblende rather than pseudomorphs after hornblende. In much of the northern section of the mine, pale biotite and calcite derived from the alteration of hornblende are scattered through the alteration zone with only occasional segregations after hornblende. That the biotite and calcite are after hornblende is clearly shown where fractures, filled with sulfides, cut across amphibolite normal to the strike of the amphibolite banding producing the same alteration effects (Fig. 2a).

The β index of refraction of the forty specimens of biotite from various points in the mine showed that the Fe : Fe + Mg ratio ranged between .23 and .40 irrespective of the composition of the hornblendes (Fe : Fe + Mg range of .38 to .61, based on fifteen specimens) from which the biotites were derived. Of these forty samples of biotite, only eight had Fe : Fe + Mg ratios between .34 and .40, and in each case these biotites were at the outer

edge of alteration. In the one systematic traverse of β index determinations, the Fe : Fe + Mg ratio showed a decrease from .40 at the outer edge of alteration to .28 at the inner edge, seven out of nine determinations falling on a straight line plot.

Plagioclase shows only minor alteration effects in the biotite subzone. The first sign of alteration is the development of very fine-grained material peripheral to the individual grains. Where the degree of alteration is greater, the material is developed along cleavage and is coarse grained enough to be identified as carbonate intermixed with white micaceous material. Separation of the mica and subsequent X-ray study revealed a muscovite pattern.

Two varieties of chlorite are present in minor amounts within the biotite subzone. One variety is readily distinguished by its anomalous blue birefringence. It is biaxial negative with a low 2V, a β index of refraction of 1.574 and is classified by Hey (5) as pennine. The second variety is biaxial positive with a 2V range of 30 to 50 degrees, has a β index of refraction of 1.610 and is classified as corundophyllite. The two chlorites have similar Fe : Fe + Mg ratios in the range of .25 to .31 but apparently differ considerably in alumina content. Their Fe : Fe + Mg ratios are in the same range as those of associated biotite. Pennine and corundophyllite have distinctly different habits. Pennine is intimately associated with biotite and carbonate after hornblende. Where rare, it is generally present as small equidimensional flakes within carbonate after hornblende or clustered about the periphery of such grains. When more abundant, it is similarly distributed in biotite. In the lower part of the orebody at 10100N pennine forms pseudomorphs after hornblende without the appearance of biotite. When accompanying biotite, pennine is randomly distributed across the alteration envelope. Thus the average modal content of pennine in eight adjoining thin sections across the biotite subzone at 14200N is 0.45%, while in thirteen adjoining thin sections at 15000N it is 1.88%. Apart from a high content (3.63%) in a thin section at the outer edge of the biotite subzone at 14200N and a high value (14.0%) near the inner edge of the subzone at 15000N, other values are low and have no systematic relationship in respect to their positions within the zone. Pennine is absent from rocks outside the alteration envelope.

Corundophyllite is randomly distributed in the biotite subzone throughout the mine. Characteristically it forms after hornblende and biotite and replaces minerals as selvages about individual grains as well as irregular intergrowths along cleavage. This is also the habit of chlorite after biotite and hornblende outside the alteration envelope in the vicinity of the mine. The modal percentage of corundophyllite in the biotite subzone varies from .2 to 15.7 percent and averages 3.3 percent based on forty thin sections. This is approximately the range and average percentage of chlorite after amphibole in amphibolites of the district.

Magnetite and ilmenite, which are present in amphibolite, are absent inside the alteration envelope. Polished section study indicates that rutile forms after ilmenite. Rutile occurs in amphibolite and in the alteration zones as needle- or rod-like crystals, whereas rutile after ilmenite has an irregular

shape and larger size corresponding to the shape and size of the original ilmenite grains.

The above discussion has been limited to alteration within amphibolite on the footwall of the main ore zone and in the No. 3 ore zone. Gile Mountain formation schists on the hangingwall of these orebodies generally do not show as marked mineralogical changes in the zone of alteration. This results from the fact that the end point in the alteration sequence within the various rock types is sericite schist, a rock, which, in places, differs mineralogically from the rocks outside the alteration zone only in the absence of minor biotite, oligoclase, carbonate, and fine-grained carbonaceous material.[8] These minerals, with the exception of the carbonaceous material, are stable in the biotite subzone. Kyanite and garnet are both unstable within the alteration zones, and when they are absent from schists due to compositional variation, the only criterion for establishing the outer edge of alteration is the presence or absence of carbonaceous matter.

Kyanite, where present, is pseudomorphically replaced by muscovite. Two generations of almandine garnet are present in the alteration zones within schists. Those of the first generation are pseudomorphically replaced by biotite, calcite, pyrrhotite, and minor quartz. Garnets of the second generation are not accompanied by alteration products. Unlike garnets outside the alteration zones they contain poikilitically-included pyrrhotite. They are developed alongside pseudomorphs, and, in rare cases, have been noted to occur partly superimposed across the sites of the pseudomorphs after earlier garnets. The composition of these garnets was previously discussed.

Biotite in schist undergoes a compositional change across the alteration zones towards ore. The change is most noticeable when the original biotites are black. The change involves the pseudomorphic replacement of such biotite by progressively paler biotite and fine-grained pyrrhotite. The Fe: Fe + Mg ratio of biotite after garnet also decreases toward the vein.

Plagioclase and the minor calcite present in the schists are stable within the biotite subzone.

Assemblages of ferromagnesian minerals in the biotite subzone include pale biotite-garnet-chlorite, pale biotite-chlorite and chlorite.

Sericite Subzone.—Where the sericite subzone within amphibolite is perfectly developed, the zone consists of white to apple-green sericite, pyrrhotite, minor quartz, chalcopyrite, and accessory rutile and apatite. In general, the quartz content of the sericite subzone is no greater than in the biotite subzone or in the adjacent unaltered amphibolite. However, in some localities, lenticular veins of clear granular quartz are present in the sericite, and to a lesser extent, in biotite subzones. The veins may be several feet long and are invariably parallel to the adjacent bedding. Where quartz veins are present, the alteration zones contrast sharply with the adjacent amphibolite, which is generally free of such veins.

Where the sericite subzone has not reached the end point of alteration, it is generally composed of alternating bands of sericite, and sericite with varying

[8] Analyzed as carbonaceous material by J. Ito, Department of Mineralogy and Petrography, Harvard University.

TABLE 4

EZ 225–243: Composition of hornblende and of biotite rimming hornblende
EZ 273–335: Composition of biotite pseudomorphic after hornblende
Rock: Westwall Amphibolite and altered zones within Westwall Amphibolite

Number	Mean refractive index of hornbende	*mg*-number of hornblende (Foslie)[1]	$\frac{Fe}{Fe + Mg}$ ratio[2]	β index of biotite	$\frac{Fe}{Fe + Mg}$ ratio
EZ 225	1.682	34	.66	1.648	.61
EZ 338	1.676	41.5	.585	1.646	.58
EZ B51	1.671	48	.52	1.639	.52
EZ 222	1.668	52	.48	1.626	.43
EZ 318	1.667	53	.47	1.631	.46
EZ 241	1.666	54	.46	1.623	.40
EZ 243	1.659	62	.38	1.621	.38
EZ 273	—	—	—	1.658	.71
EZ 336	—	—	—	1.652	.65
EZ 216	—	—	—	1.650	.63
EZ B54	—	—	—	1.648	.62
EZ B56	—	—	—	1.648	.62
EZ 276	—	—	—	1.646	.59
EZ 335	—	—	—	1.643	.56

[1] *mg* equals $\frac{MgO}{2Fe_2O_3 + FeO + MnO + MgO}$ equals atomic ratio $\frac{Mg}{Mg + Fe + Mn}$.

[2] Approximation from the Foslie *mg*-number.

proportions of frayed plagioclase, biotite, phlogopite, calcite, and accessory minerals. This banding reflects the original banding of amphibolite in which plagioclase-rich bands have been altered to sericite, and the hornblende, calcite, and plagioclase bands have been altered to sericite, biotite, or phlogopite. Plagioclase is pseudomorphically replaced by sericite along intergranular boundaries so that in those instances where alteration is not complete, small frayed plagioclase grains remain in a matrix of sericite laths up to .07 mm long. Where plagioclase is zoned, the more calcic cores are altered to an extremely fine-grained material that yields a calcite and muscovite X-ray diffraction pattern. Selective alteration along cleavage and twin planes is only evident in the calcic cores of individual grains.

Biotite is replaced by unit pseudomorphs of sericite. Colorless to nearly colorless phlogopite and finely-divided pyrrhotite appear as an intermediate phase in this change. Both the replacement of biotite by phlogopite and phlogopite by sericite take place along cleavage planes and grain boundaries. Colorless phlogopite may be distinguished from sericite either by the presence of poikilitically-included fine pyrrhotite or by its uniaxial figure. In the replacement of phlogopite by sericite, poikilitically-included pyrrhotite is largely shed to intergranular positions.

The sericite subzone varies in color from silvery white to dark green due to the presence of chromium in the sericite. The chemical analysis[6] of apple green sericite, its formula and optical data are presented in Table 5. The analysis of garnet from the same rock is presented in Table 1. The sericite was hand-picked under binocular microscope and was free of any traces of garnet, sulfide, rutile, biotite, and soluble carbonate. Impurities

[6] Analysis by J. Ito, Department of Mineralogy and Petrography, Harvard University.

TABLE 5

CHEMICAL ANALYSIS OF CHROMIAN SERICITE FROM GARNET-SERICITE SCHIST (EZ 329) WITHIN THE WESTWALL AMPHIBOLITE

Coordinate position, 9500N, Pit No. 2, Elizabeth mine, Vermont.
Analyst—J. Ito, Harvard University.

	Weight, %
SiO_2	45.88
Al_2O_3	35.19
Fe_2O_3	0.26
FeO	0.75
MnO	—
MgO	1.25
CaO	1.04
Cr_2O_3	0.38
TiO_2	0.46
Na_2O	0.85
K_2O	9.18
H_2O	4.70
	99.94

Chemical formula of sericite:

$$(K_{.78}\,Na_{.11}\,Ca_{.02})_{0.96}\,(Al_{1.78}\,Fe_{.04}\,Fe_{.01}\,Mg_{.12}\,Cr_{.02}\,Ti_{.02})_{1.99}$$
$$(Al_{.98}\,Si_2O_5)_4\,O_{0.81}\,(OH)_{2.07}$$

Refractive indices:

$$\left.\begin{matrix}\alpha = 1.562\\ \beta = 1.588\\ \gamma = 1.596\end{matrix}\right\} \pm .02$$

are thought to have been less than one-half of one percent plagioclase and quartz.

The sericite subzone in Gile Mountain formation schists show little variation from the sericite subzone within amphibolite.

Stage 3 Alteration (Post-ore)

Chlorite Subzone.—At the outer edge of alteration, the ferro-magnesian minerals, hornblende, garnet, and biotite are pseudomorphically replaced by chlorite, carbonate, epidote, sphene, fine blade-like grains of quartz, and pyrrhotite. The outlines of the pseudomorphs after hornblende are perfectly preserved toward the vein as far as the sericite subzone, the only change in the pseudomorphs being the pseudomorphic replacement of sphene by skeletal grains of rutile. Biotite, where present, is replaced by unit pseudomorphs of chlorite, and fine pyrrhotite. Garnet is replaced by pseudomorphs of chlorite, carbonate, pyrrhotite, and quartz. The chlorite is pennine in all cases.

Plagioclase is largely unaltered. Extremely fine sericite is present along grain boundaries peripheral to individual grains of plagioclase and in this respect is similar to stages 1 and 2. Calcite shows a considerable increase toward the vein.

Ilmenite is stable at the outer edge of alteration, but toward the vein it is pseudomorphically replaced by pyrrhotite and skeletal grains of rutile.

Sericite Subzone.—The partial or complete replacement of silicate minerals by sericite in no way differs from the sericite subzones of stages 1 and 2.

However, the grain size of the alteration products is substantially finer. Epidote, sphene, and rutile are absent at the veinward edge of alteration. Although plagioclase may be completely replaced by a fine-grained felted mass of sericite, chlorite after hornblende and calcite generally persist in substantial amounts in this subzone. Estimated modes indicate that chlorite is present to the extent of 20 percent compared to 50 percent in the chlorite subzone, and calcite is 8 percent compared to 26 percent.

Unlike either stages 1 or 2, the sericite subzone of stage 3 is marked by pronounced silicification at the veinward edge of alteration. Estimated modes across one alteration zone indicate that quartz in amphibolite amounted to less than 1 percent, while the chlorite subzone contained approximately 3 percent and the sericite subzone up to 33 percent.

Traces of pyrrhotite and chalcopyrite are present across the alteration zones in the sericite subzone and may constitute over 1 percent of the rock at the veinward edge of alteration. No sulfide veins have been found associated with stage 3 alteration. A "vein" may be a shear or a barren quartz vein several inches in width.

CHEMICAL CHANGES AND CORRESPONDING MINERALOGICAL CHANGES

Tables 6 and 7 are diagrams showing chemical variations and modal distribution of minerals across an alteration zone within amphibolite in stage 2 alteration adjacent to the ore. Figure 3 shows the relationship between the cross-section studied, structure and ore zone. Because of original compositional variation, it is necessary, when interpreting the chemical variation diagrams (Table 7, to refer to Table 6 for variation in the modal percentage of minerals. Plagioclase, hornblende, and calcite make up to 96 percent of the constituent minerals of amphibolite, and separate plots of the modes of these three minerals versus distance across amphibolite should be horizontal if compositional variation is negligible. In the biotite subzone of alteration, similar plots of plagioclase plus minor sericite, hornblende plus biotite plus chlorite and of calcite should likewise be horizontal if compositional variation is negligible. However, as can be seen from Table 6, compositional variation does occur across the traverse studied although in no systematic manner. In the sericite subzone composed largely of sericite and sulfides, there is no way in which compositional variation of the original amphibolite can be evaluated.

The chemical variation diagram shows a large change in potassium and smaller changes in other components in the biotite subzone as compared to amphibolite. The sericite subzone, however, shows a drastic change in which sodium, calcium, and magnesium decline to small values at the vein edge. On the other hand, potassium, total iron, sulfur, and copper (Fig. 4) show marked increases.

Mineralogically, the step-like increase of potassium in the biotite subzone corresponds to the pseudomorphic replacement of hornblende by biotite and to the development of a minor amount of sericite after plagioclase. The gradual increase of potassium across this zone is due to (a) stability of a minor amount of hornblende in the outer part of the zone, and (b) original

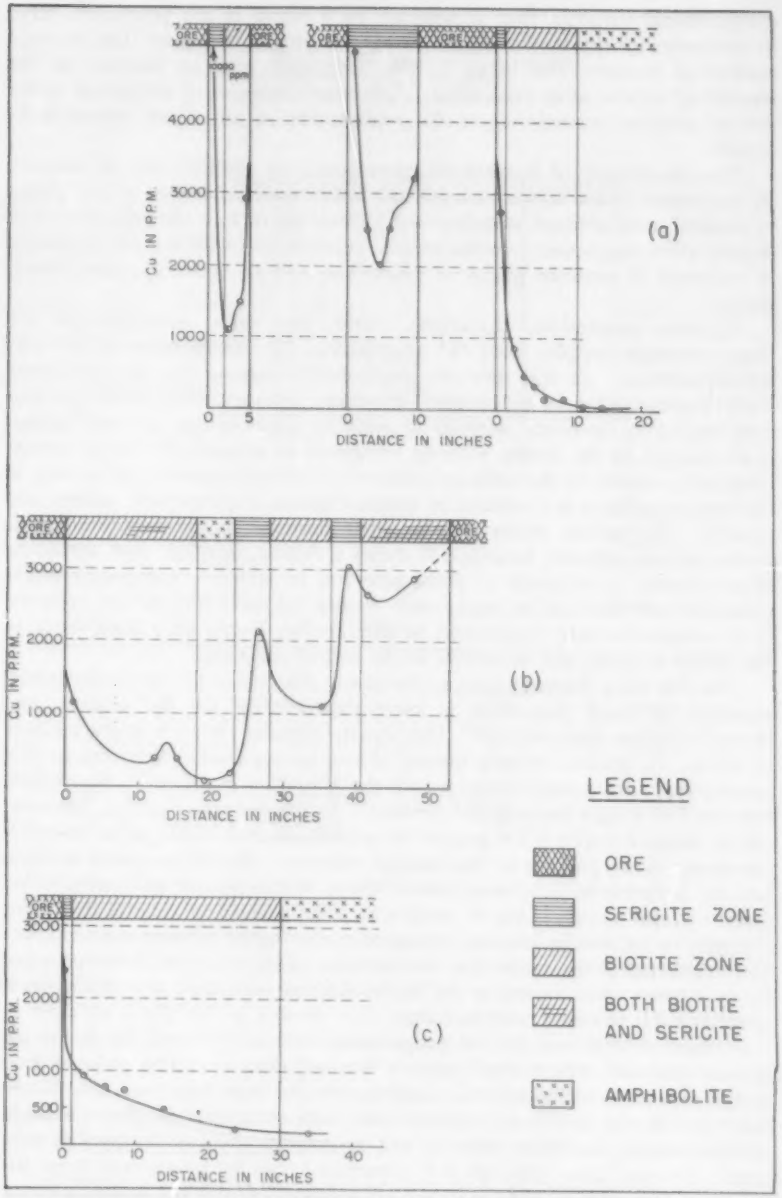


FIG. 4. Copper distribution curves in the wallrock of the Elizabeth mine: (a) in the wallrock in the No. 3 drift at 14200N, 975 level; these data correspond with other chemical data presented in Table 7; (b) in an alteration zone developed in a bed of amphibolite bounded by ore on either side. Section from the 1400 sublevel at 9910N; (c) in the wallrock in the No. 3 drift, at 15000N, 975 level.

compositional variation that is reflected by a hump in the potassium curve in the center of the biotite subzone corresponding to a higher than average content of biotite. The hump is also associated with an increase in the amount of sericite after plagioclase. The sharp increase of potassium in the sericite subzone corresponds to the replacement of all silicate minerals by sericite.

The breakdown of hornblende corresponds to a slight loss of sodium. In the center of the biotite subzone the lower sodium content is due partly to original compositional variation and also an increase in the replacement of sericite after plagioclase. In the sericite subzone, the only sodium remaining is contained in remnant grains of plagioclase and as minor amounts within sericite.

Calcium, magnesium, chromium, sulfur, and silica determinations are based on single samples from (1) amphibolite, (2) biotite subzone, and (3) sericite subzone. In that they are single determinations they are not necessarily representative of a subzone. However, interpretation of the analysis with regard to the modal analysis of minerals suggests that calcium content is unchanged in the biotite subzone compared to amphibolite but is almost completely absent in the sericite subzone. The only calcium remaining in the sericite subzone is contained in remnant grains of plagioclase, calcite, and sericite. Magnesium shows only a slight decrease in the biotite subzone. In the sericite subzone, however, it shows a drastic decrease, that remaining being present in remnants of phlogopite and in sericite. Chromium determinations are identical in amphibolite, biotite subzone, and sericite subzone. It is contained within hornblende, in amphibolite, biotite after hornblende in the biotite subzone, and in sericite in the sericite subzone.

The low silica determination in the biotite subzone is due to compositional variation in which plagioclase is lower than average for the subzone, and biotite is higher than average. The sericite subzone shows a slight increase in silica. In general, quartz content shows no systematic variation in thin section study from amphibolite across the alteration envelope to the sericite subzone and ranges between 0–5 percent. In the traverse A_{16}–A_{18}, however, quartz varies between 0–1.6 percent in amphibolite and biotite subzones while increasing to 11 percent in the sericite subzone. Based on modal analysis and the presence of occasional quartz lenses in the sericite subzone avoided in thin section selection due to their size, it is believed in general that silica is higher in the sericite subzone compared to the biotite subzone and amphibolite. Although it is possible that this increase in silica content is compensated for by a lower silica content in the biotite subzone compared to amphibolite, it is not possible to detect such a change.

Values of total iron fall off progressively toward the vein, as far as the sericite subzone, where they show a marked increase. The gain of iron in the sericite subzone approximately equals the iron loss from the biotite subzone. Modal sulfide (pyrrhotite and minor chalcopyrite) shows a slight increase across the biotite subzone and a sharp increase in the sericite subzone. Ferrous iron, although not determined, can be interpreted from the Fe : Fe + Mg ratio of biotites to fall off veinward across the biotite subzone and decrease sharply in the sericite subzone, coincident with the pseudo-

TABLE 5

TRAVERSE OF ESTIMATED MODES AT THE 14200 N CROSS-SECTION, NO. 3 DRIFT 975 LEVEL
SEE FIGURE 3 FOR DETAILED LOCATION

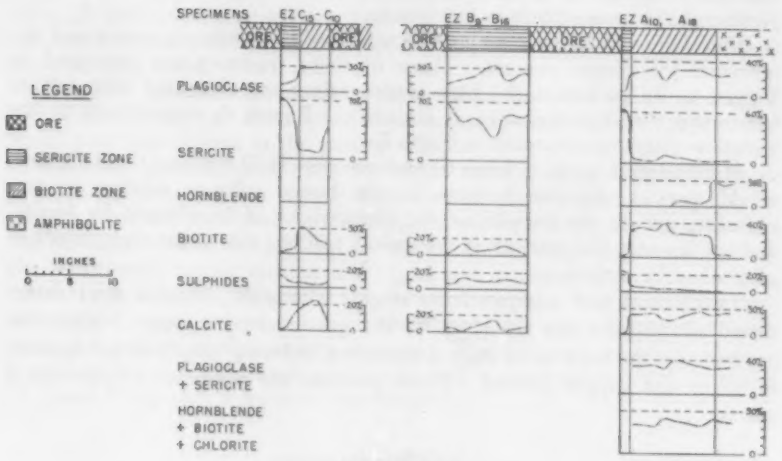


TABLE 6

	(1) Amphibolite	(2) Sericite-biotite-garnet schist	(3) Sericite schist
	Weight %	Weight %	Weight %
K_2O	0.55– 1.01	4.29	7.52
Na_2O	3.88– 4.78	2.73	1.92
CaO	14.46–19.95	3.26	2.01
Total Fe	7.58– 8.04	6.68	7.11
S	0.00– 0.27*	0.57	1.07

* Calculated from the range of modal pyrrhotite and chalcopyrite in amphibolite.

morphic replacement of biotite by phlogopite and phlogopite by sericite. It it apparent that only part of the released iron is fixed as sulfide across the biotite subzone, the remainder being fixed in the sericite subzone.

Sulfides identified in altered wall rock include pyrrhotite, chalcopyrite, and rarely sphalerite. Blades of cubanite within chalcopyrite have been noted in the larger grains. Pyrrhotite and chalcopyrite may be detected in trace amounts within rocks away from the mine.[7] The background copper content of eleven samples of amphibolite from widely separated points ranges from 24 to 223 ppm and averages 109 ppm. In the study of three of these samples,

[7] The distribution of copper was studied jointly by R. E. McCrehan and the author. The bulk of the samples studied (52 out of 58) were supplied by the author, while the copper determinations were carried out by McCrehan with the author assisting. The data are tabulated in a thesis by McCrehan (7, pp. 23–32).

McCrehan separated hornblende from the specimens (approximately 60% hornblende) and estimated the copper content to be 45, 72, and 36 ppm. The corresponding copper contents of the whole of the corresponding rock samples were 94, 137, and 85 ppm, respectively. Polished sections of the specimens revealed pyrrhotite in all three specimens and chalcopyrite in two specimens. Neither sulfide was evident in hornblende.

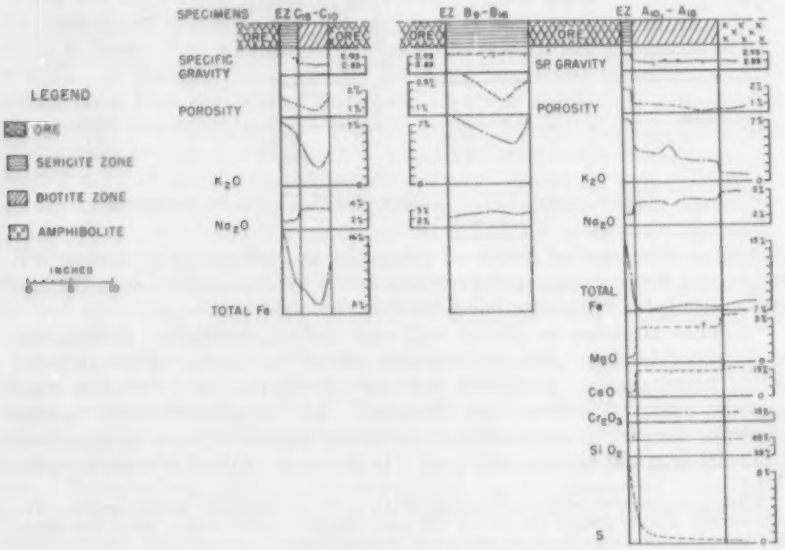
Five series of samples were collected from the alteration zones and determined for copper content. Three of these traverses are presented in Figure 4. In each case, the high copper values are associated with sericite bands and the veinward edge of alteration. Figure 4a corresponds to the variation diagrams presented in Table 7.

Mineralogical modes (Table 6) indicate that H_2O content, if determined, would show a step-like increase in the biotite subzone relative to amphibolite, due to the pseudomorphic replacement of hornblende by biotite, and another step-like increase in the sericite subzone due to the replacement of plagioclase by sericite.

Two partial rock analyses from stage 1 alteration subzones were determined and showed that the chemical changes involved in stage 1 alteration are basically the same as in stage 2 alteration, differing largely in the amount of sulfur and copper present. These analyses are presented in columns 2 and 3.

TABLE 7

CROSS-SECTIONAL TRAVERSE AT 14200 N CROSS-SECTION, NO. 3 DRIFT 975 LEVEL SHOWING CHEMICAL COMPOSITION OF WALL ROCK IN WT. %. SEE FIGURE 3 FOR DETAILED LOCATION.



The samples from which the partial chemical analyses in columns 2 and 3 were determined were taken from the 12500N cross-cut in the west wall of the 750 sublevel drift. The rock in column 3 represents the most advanced degree of alteration. Column 1 shows the range of values of several partial analyses of representative amphibolite samples from within the mine, and although none of the samples is from the 750 sublevel cross-cut, the values presented represent the probable range of composition that the amphibolite is likely to have at that point.

The only apparent difference in these values from the values of stage 2 (see Table 7) are (a) appreciably lower sulfur content, and (b) appreciably lower total iron content in the sericite subzone.

The only chemical determinations of the rocks of stage 3 alteration were titanium and copper. The copper dispersion pattern is similar in shape to the pattern presented in Figure 4c. Although the shape of the curves is similar, the contained copper is radically different. In the stage 3 pattern studied, the background copper content is 50 ppm and increases toward the vein to a maximum value of 259 ppm in the sericite subzone. This is in sharp contrast to the copper curves of stage 2 alteration which reach several thousands parts per million in the sericite subzone. The fractures to which stage 3 alteration is in places related are barren, and a single copper determination of quartz filling such a fracture was 40 ppm.

INTERPRETATION OF DATA

The metasomatic changes in the wallrock of the Elizabeth orebodies are consistent with an epigenetic origin of the ores introduced as sulfides or sulfide complexes, together with other constituents, in the medium of a solution. Some features that distinguish the alteration envelope about the Elizabeth orebodies from the unaltered wallrock are (1) bleached haloes, (2) increased hydration toward the vein, (3) addition of potassium, copper and sulfur to the wallrock, (4) removal of many rock components, notably sodium, calcium, magnesium, and carbonaceous matter, and (5) increased porosity and permeability toward the vein.

It is proposed that sites now occupied by ore were highly permeable zones between flexed bedding planes and breccia zones at the contact of amphibolite and mica schists, and that solution migrated outward from such vein channels by capillary action. Rapid variation in the widths of alteration suggests that contemporaneous deformation of the wallrocks during the introduction of solutions increased permeability of wallrocks and allowed circulation of solution through certain zones that effectively widened the zones of solution-saturated rock. The symmetrical zones of alteration in such solution-saturated wallrock can be explained by diffusion of ions from the vein solution through the solution filling available pore space and capillary openings.

The uniformity of the copper distribution patterns and their close similarity to theoretical diffusion curves in a homogeneous substance suggests that diffusion was an important factor in rock alteration. Copper and sulfur have erratically high values in the sericite subzone in some places where

porosity shows as much as a nine-fold increase, and permeability as much as one hundred-fold increase, over that of the unaltered wallrock. The facts suggest that such values are due to greater ease of diffusion of copper and sulfur complexes into zones that have high porosity and permeability.

The sulfur profile reflects the amount of sulfur fixed in chalcopyrite and pyrrhotite, both of which increase toward the vein. With the increase of sulfides across the biotite subzone toward the vein, total iron decreases. This indicates that only part of the iron released during the pseudomorphic replacement of hornblende by biotite is fixed as pyrrhotite and chalcopyrite; the remainder had diffused veinward to the more porous and permeable sericite subzone where sulfide activity was sufficiently high to fix migratory iron as pyrrhotite and chalcopyrite.

The step-like increase in potassium across the alteration envelope toward the vein is consistent with diffusion of potassium into the wallrock. The step-like increases that are coincident with the appearance of a potassium-bearing mineral after a nonpotassium-bearing mineral represent points at which the activity of potassium was sufficiently high for a particular pseudomorphic replacement of one mineral by another to proceed. The particular mineral that forms (biotite or chlorite after hornblende) and its exact composition would be dependent on the activities of other components, the bulk compositional changes due to alteration and to the PT conditions prevailing at the time of replacement. The Fe: Fe + Mg ratio of the biotites in the alteration process were evidently affected by sulfide activity. Thus the biotites of stage 1 alteration, which is accompanied by only trace amounts of pyrrhotite, have Fe: Fe + Mg ratios close to the Fe: Fe + Mg ratios of the hornblendes they replace. On the other hand, the Fe: Fe + Mg ratios of biotites in stage 2 alteration, which is accompanied by abundant pyrrhotite and chalcopyrite, are very much lower. The biotite present in the alteration section A_{10} to A_{18} in Figure 3 shows a decrease in the Fe: Fe + Mg ratio toward the vein. The presence of increased amounts of pyrrhotite and chalcopyrite toward the vein suggests that the sulfide activity during alteration had a controlling influence on the Fe: Fe + Mg ratio of biotite which formed after hornblende or garnet. A further indication of this point is the appearance of colorless phlogopite as an intermediate phase in the pseudomorphic replacement of biotite by sericite in the sericite subzone. This is coincident with a large increase in pyrrhotite and chalcopyrite content and suggests that a substantial increase in sulfide activity resulted in a removal of iron from the biotite.

Although silicification is not present in either stage 1 or stage 2 alteration, lenticular veins of quartz are peculiar to the alteration zones. These quartz veins are believed to represent silica released from the alteration processes and precipitated as quartz in lentils parallel to bedding planes. Stage 3 alteration, in contrast to stages 1 and 2, shows pronounced silicification at the vein edge. Without chemical analysis, it cannot be ascertained whether the silicification represents an introduction of silica or the precipitation of veinward-migrating silica released during alteration. However, it is believed that stage 3 alteration represents the last phase of alteration effected under lower metamorphic

PT conditions than the preceding stage, and as such silicification is common to the lower temperature type of alteration.

Metamorphic Conditions During Alteration.—The encroachment of alteration zones across metamorphic rocks with resultant pseudomorphic replacement of kyanite, hornblende and garnet by hydrous silicates indicates that progressive metamorphism had reached its thermal peak before the commencement of local hydrothermal activity. The effect of alteration on amphibolite changed its bulk composition from that of a basic rock to that equivalent to a ferromagnesian-poor pelitic schist adjacent to the ore (sericite subzone) and, in the intermediate step (biotite subzone), to a calcareous pelitic schist. The distribution of ferromagnesian minerals in the outer sub-

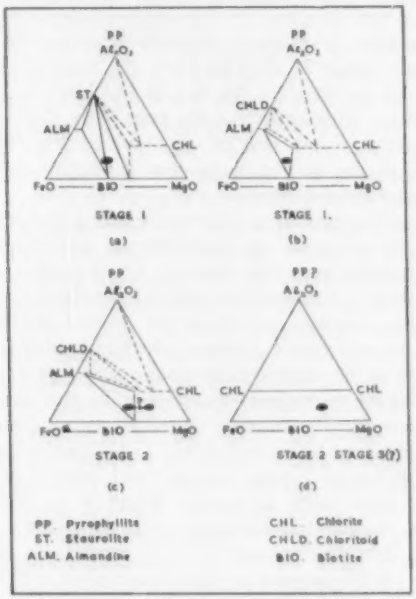


FIG. 5. AFM phase diagrams showing the mineral assemblages common to outer subzone of alteration. The dark areas represent the bulk composition of the altered amphibolite.

zone of alteration is as follows: stage 1 biotite subzone, dark biotite-garnet-chlorite, and to a minor extent dark biotite-garnet-staurolite and dark biotite-staurolite; stage 2 biotite subzone, pale biotite-garnet-chlorite, pale biotite-chlorite and to a minor extent chlorite; stage 3 chlorite subzone, chlorite.

The presence of staurolite and second generation garnets in the alteration zones indicates that hydrothermal activity ceased in stage 1 alteration zones when the metamorphic conditions were at least equivalent to that of staurolite grade; metamorphism having reconstituted the alteration products to their

present assemblages. The other assemblages cited are likewise thought to represent minerals that formed or were stable under the decreasing metamorphic temperature and pressure prevailing when hydrothermal activity ceased in certain zones within the two mile length of the known orebody, and in its immediate vicinity.

The mineral assemblages and their interpreted relation to the metamorphic zones in Vermont are shown on AFM phase diagrams [8] (Fig. 5). The assemblage biotite-garnet-chlorite is not present in the staurolite zone and, in terms of known assemblages of the region, reflects a lower metamorphic grade. The difference between the assemblage biotite-garnet-chlorite in stages 1 and 2 lies in the Fe : Fe + Mg ratio of the biotite and chlorite, the bulk composition of the ferromagnesian content being constant if sulfides are taken into account.

The stage 2 alteration assemblage of biotite-chlorite reflects an assemblage of lower metamorphic grade as the Fe : Fe + Mg ratio of biotite and chlorite are in the same range as those of the biotite and chlorite in the assemblage biotite-garnet-chlorite. This rules out the possibility that the biotite-chlorite assemblage is a compositional change (queried in Fig. 5c) due to either metasomatic effects of the alteration process or variation in the bulk composition of the original amphibolite.

It is believed that Figures 5a to d are evidence of decreasing metamorphic PT conditions at the cessation of hydrothermal activity in various areas. Whether or not alteration persisted through lower grades of metamorphism is not clear. The only ferromagnesian mineral identified in stage 3 alteration was pale to colorless chlorite, but from the limited study of this type of alteration, it was by no means certain whether colorless phlogopite was present as is the case in the sericite subzone of stage 2 alteration.

There is no evidence to support the possibility that the various mineral assemblages represent various degrees of metasomatic alteration at constant or approximately constant PT conditions. The assemblages change from one to another as shown in Figure 5 in a zonal pattern along the strike of the alteration zones from south to north. There is no zonal pattern as described above across the biotite subzone of alteration, although the decreasing Fe : Fe + Mg ratio of biotite toward the vein appears to be metasomatic in origin. This change is interpreted as due to increased sulfide activity toward the vein, a view supported by the fact that sulfide content of the biotite subzone increases toward the vein and largely compensates the change in terms of bulk composition.

The zonal alteration pattern described is reflected by the zoning of sulfides in the orebodies. In the southern section of the mine where the ore has a high Fe : Cu ratio the assemblage pale biotite-garnet-chlorite is common in the biotite subzone of alteration, while in the northern section of the mine the much lower Fe : Cu ratio is associated with pale biotite-chlorite assemblage. Chlorite alteration is associated with a lower Fe : Cu ratio again. In places it is associated with veinlets composed of chalcopyrite alone. An

[8] Phase diagrams show assemblages common to Vermont. Notes from lectures on metamorphism by J. B. Thompson.

analysis of sphalerite by X-ray spectroscopy[9] indicates a temperature of formation of 325° C. The corresponding ferromagnesian assemblage in the biotite subzone is pale biotite-chlorite. It is anticipated that an analysis of sphalerite accompanying a pale biotite-garnet-chlorite assemblage would indicate a temperature higher than 325° C and sphalerite accompanying chloritic alteration would be lower.

Relation of Alteration to Deformation.—Textural relations of porphyroblastic minerals contained in the metamorphic rocks of the area indicate that the thermal peak of metamorphism occurred before the peak of the accompanying deformation that formed the Strafford dome and associated structures. Hornblende of the fine-grained amphibolites shows a preferred orientation, lying parallel to the bedding planes even in the apical position of folds, and the author has noticed no b-lineation in the vicinity of the mine. The suggestion is that the hornblende grew by mimetic crystallization. Where amphibolite is medium- to coarse-grained, hornblende shows a random orientation although some grains are rotated as much as 15 degrees. Likewise garnet shows little or no rotational effects in the metamorphic rocks of the area.

In strong contrast to these features, second generation garnets present in the alteration zones show marked snowballing to an observed maximum of 120 degrees. The suggestion is that deformation was weak during progressive metamorphism (early structure[10]) but was strong ("Christmas-tree" structure[10]) during the declining stages during which alteration occurred.

Such a view gives a logical explanation of the distribution of stages 1, 2, and 3 alteration zones. Stage 1 alteration is largely confined to amphibolite, the most permeable common rock of the Gile Mountain formation. The alteration has a random distribution in relation of fold structures and is unrelated to faults and shears, and is interpreted to have occurred after the thermal peak of metamorphism but before the main onset of deformation associated with the formation of the Strafford dome structure.

Ore and accompanying stage 2 alteration is related almost entirely to fold positions and to limbs between successive folds. Ore and accompanying alteration related to veinlets is a minor feature. The presence of staurolite and snow-balled second generation garnets in stage 1 alteration zones suggests that flexing and folding of the rocks during the formation of the Strafford dome structures caused highly permeable zones to develop in fold positions, thus causing solution flow to be diverted from amphibolite to more permeable zones in fold positions at the contact of amphibolite and Gile Mountain formation schists.

To a minor extent, stage 3 alteration has common loci with stage 2 alteration. In general, however, it is largely controlled by post-ore faults, shears and shear zones in areas lateral to the orebodies and their accompanying alteration.

[9] Specimen EZ 42 (pyrrhotite-chalcopyrite-sphalerite-cubanite) from section 15015N, elevation 585 feet. Iron content was determined as 6.7% Fe but awaits confirmation by comparison with further standards.

[10] Discussed in Part I.

CONCLUSIONS

The alteration zones were formed by diffusion of ions into wallrock from a solution of approximately constant composition during decreasing metamorphic temperatures and pressures. The subzones in the alteration envelopes are thought to have developed contemporaneously, their mineralogical differences to be due both to decreasing ion activities lateral to the permeable channelways and to the prevailing temperature and pressure conditions at the time of alteration. Thus muscovite formed after plagioclase in all three stage of alteration as a result of high potassium activity, whereas temperature and pressure apparently controlled the pseudomorphic replacement of hornblende and garnet by either (a) biotite and minor chlorite or (b) chlorite alone.

Metamorphic temperature and pressure conditions existing when hydrothermal activity ceased reconstituted the mineral assemblages and gave rise to the metamorphic index minerals staurolite and garnet within the alteration envelopes.

ACKNOWLEDGMENTS

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BROKEN HILL,
NEW SOUTH WALES, AUSTRALIA
Dec. 15, 1958

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AMYGDULE MINERAL ZONING IN THE PORTAGE LAKE LAVA SERIES, MICHIGAN COPPER DISTRICT

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PART II (*Continued from last number*)

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AGE AND ORIGIN OF THE AMYGDULE MINERALS AND COPPER

Discussion of the age and origin of the amygdule minerals is best introduced by a consideration of the hypotheses advanced by earlier writers. Butler and Burbank (13) dealt only briefly with the origin of the amygdule minerals exclusive of copper. The chemicals forming these minerals and the associated rock alteration minerals were believed to be derived by hydrothermal waters from the flows themselves (13, p. 53 and 107–108). The copper is specifically ascribed to a magmatic source (13, p. 124), brought to its present site by the same hydrothermal solutions that followed the more permeable channelways of the lavas and conglomerates. Broderick's work on the differentiation of the Kearsarge flow (9) dealt only to a limited degree with the amygdaloidal flow top and its minerals. The albitic nature of much of the flow top was not discussed. The chemical analysis of the section of the flow 12 to 24 feet from the top showed a high concentration of iron, soda, potassium, titanium, phosphorous, sulfur, and copper. This enrichment was ascribed to the transfer of these substances as volatile material during crystallization. The soda-rich flow top (albite-basalt of the present paper) is, under this hypothesis, of magmatic (deuteric) origin. The high ferric iron and low ferrous iron of the flow top was also ascribed to deuteric processes.

Cornwall (16, 17) has written extensively on the origin of the copper and the petrology of the flows of the Keweenawan series. Several of his views are at variance with those of Butler and Burbank and those of Broderick. Cornwall believes not only that the albite diabase of the flow top is a product of magmatic differentiation due to reaction with vapor (16, p. 192) but he implies that many of the amygdule minerals were deposited at an early date during or soon after the consolidation of the flows (16, p. 192–194). Cornwall (16; 22, p. 619–620) believes the copper was collected from the flows themselves.

Niggli (42) has stated that the differentiation of the lavas of the Portage Lake lava series tends toward development of a spilitic association. Amstutz

(2) considers that spilites are primary magmatic crystallization products formed under hydromagmatic conditions. He (1) has discussed formation of copper minerals from spilitic magmas with special reference to the lavas of Glarus, Switzerland. In considering many occurrences of splitic mineral assemblages Amstutz (2) concludes that the habit and close association of monomineralic mineral deposits with spilitic rocks illustrates the fact that these mineral deposits are spilitic differentation products.

With respect to the chemistry of the copper deposition, there is also a difference of views. Cornwall follows Lindgren (39, p. 418), in suggesting that the native state of the copper may be due to loss of sulfur at the time the lava is extruded. Broderick (10, p. 711) and Butler and Burbank (13, p. 129–137) believe the oxidation of sulfur to sulfate by ferric oxide in flow tops caused deposition of native copper rather than copper sulfide. Cornwall (22, p. 621) suggests that connate waters with a high chloride content may have been driven upward by heating and crushing at depth to produce an ore-bearing solution.

The evidence in the present paper corroborates some of these conclusions, amplifies others, and suggests some differences in interpretation. Briefly, the various lines of evidence support an origin of the amygdule minerals by regional hydrothermal [6] metamorphism of the lavas and conglomerates after they were tilted. Copper is believed to have been deposited as a part of this widespread alteration process. The evidence suggests that the metamorphic alteration took place during the period of folding and thrusting of the lavas of Keweenawan age. Only minor alteration of the flow tops is attributed to the period when the lava was cooling and crystallizing. Evidence as to whether the altering solutions had a magmatic source is inconclusive.

The present study contains some new information as to the time of formation of the minerals of the flow top. Two lines of evidence, the relationship of the amygdaloid mineralogy to the regional geology and geothermometric studies of quartz from the Kearsarge flow top, indicate that there has been widespread deposition of minerals after the lavas and overlying Keweenawan rocks were extruded and tilted. In the part of the Keweenaw Peninsula in which mineral zones have been delineated, boundaries of the mineral zones cut diagonally across stratigraphic horizons (Fig. 7), indicating that the amygdules were filled after the lavas were deposited. A similar lack of conformity of the boundaries of mineral habit zones and stratigraphic horizons has been advanced as evidence that the amygdule filling took place after all the flows were extruded in County Antrim, Ireland (52). The geothermal gradient of the quartz and calcite amygdules indicate further that the amygdules were filled after the lavas were tilted.

Fissures that cross the Kearsarge amygdaloid and contain carbonate, copper, and arsenical copper minerals are believed to be later than the amygdule fillings as discussed in an earlier section. The fact that these fissures are of diastrophic origin and probably related to the Keweenaw fault indicates that the amygdule filling occurred before the end of the folding and overthrusting,

[6] Hydrothermal is here used in its original sense and as defined in Webster's New International Dictionary, second edition, as "hot water."

if one assumes that the fissures were filled while the rocks were still being deformed. A comparable argument with respect to the date of the copper deposits was advanced by Butler and others (13, p. 53–55) with somewhat less supporting evidence than we now have.

Evidence in this paper supports the hypothesis that the amygdule minerals are of hydrothermal origin. The liquid inclusions in both quartz and calcite (Table 3) suggest the presence of hydrothermal liquids at the time of deposition at temperatures between 133° C and 360° C, and perhaps higher depending on the correction for rock pressure. As suggested in a previous section, the banding of amygdule mineral assemblages in the Kearsarge flow top is also compatible with an origin ascribed to hydrothermal fluids ascending along the most permeable channel, which in this locality is the Kearsarge amygdaloid. Banding of amygdule mineral assemblages similar to that in the Kearsarge amygdaloid was noted in drill core of the Evergreen flow top and in several flows just above the Kearsarge flow. Banding that involves fewer mineral assemblages was noted in a great many drill cores; the upper part of flow tops have amygdules filled with epidote and calcite and, in the stratigraphically lower part of the tops, the amygdules are filled with epidote or chlorite and quartz, and the groundmass is wholly or partly pumpellyitized.

Briefly stated, chlorite and microcline, then epidote and quartz were deposited, and finally calcite filled openings left after the temperature had decreased. This suggestion is upheld by the calcite inclusion temperatures which are much lower than those of the quartz (Table 3). The paragenetic sequence observed in single specimens, namely chlorite and feldspar, followed by epidote, quartz, and calcite (generally in that order), is also in line with the mechanism suggested.

Mineral formation in the amygdular flow tops and conglomerates was regional in extent. No vesicles that are completely empty have been seen among the enormous number observed. The only empty ones reported from the lavas of the Keweenawan series are in a drill log of a copper prospect at Knife River, Minnesota (47, p. 131 (at 106–107.5 feet)). At the outcrops in the vicinity all vesicles are filled. We believe that only a regional process could accomplish this. As mentioned earlier, almost every flow top, whether or not mined for copper, contains one or more of the minerals epidote, quartz, or prehnite as well as calcite. The quartz, epidote, and prehnite zonal pattern appears to extend throughout the lava flow tops and conglomerates of the Keweenawan series. The regional aspect of the zoning pattern discussed here gives it a significance different from that of the zoning pattern described by Broderick (7), which is based essentially on the minerals found in ore deposits.

Regional differences in mineralogy were probably caused, to a considerable extent, by original differences in temperature on a regional scale. The suggestion that prehnite is formed at lower temperatures than epidote has been made by Barth (3, p. 257). The wide overlap in the area of occurrence of these two minerals indicates that other factors are also involved and that their fields of stability surely overlap, but temperature differences are presumably a factor in their regional distribution. The prehnite-free area of the

southwestern part of the Portage Lake lava series and the epidote-free northeasterly part of this series may represent respectively hotter and cooler areas of hydrothermal activity. A temperature increase with depth in the lavas is suggested in the Kearsarge mines by the inclusion thermometric studies (Table 3). The regional pattern of the mineral occurrences and suggestions of a regional variation in temperature during mineralization of the flow tops lead to the conclusion that the amygdule minerals of the flow tops and conglomerates were produced by hydrothermal activity of regional extent, which could be termed regional hydrothermal metamorphism.

Perhaps the most fundamental contribution of this paper is the demonstration that copper in both conglomerates and amygdaloids has a place in the regional zoning pattern, and by inference, that the deposition of copper is a consequence of the processes and conditions involved in the regional hydrothermal metamorphism.

Chemical Changes in the Kearsarge Amygdaloid

The chemistry of the process by which copper and amygdule minerals are formed is suggested by chemical data for the Kearsarge flow top. As stated above, the top comprises pumpellyitized groundmass, albitized groundmass, and minerals filling vesicles and interfragmental spaces. In summary, the chemical data suggest that waters bearing carbon dioxide and calcium oxide pumpellyitized part of the flow top, albitized other parts, and freed elements that formed silicates and copper by replacement and as open-space fillings. The chemical evidence, supported by the physical position of the amygdule minerals, indicates that the whole process may have been triggered by introduction of hot carbon dioxide-calcium oxide waters, which first produced pumpellyitization. Chemicals freed from the pumpellyitization process induced albitization of the normal basalt of the flow top and contributed material for amygdule filling. Albitization may have provided some chemicals for pumpellyitization, but more likely it merely added to the chemicals needed for the amygdule minerals. At least some of the copper was derived from the flow tops and sufficient volumes of basaltic flows may have been altered at depth to provide the minable concentrations of copper in the open channelways of the conglomerates and flow tops.

Samples of the Kearsarge flow top that contain each of the several characteristic mineral assemblages were analyzed by a rapid analysis technique (48). Samples were taken from a section of the Kearsarge amygdaloid that showed typical banding of the mineral assemblages (Fig. 9A). Two samples were analyzed from each specimen, one representing the whole rock, including the amygdule fillings, and the other representing rock from which the amygdule and interfragmental filling minerals were carefully removed. Samples 2 through 4 and 6 through 8 in Table 4 are analyses of albite basalt including the amygdular minerals. These samples show marked variation in some chemical components, mainly due to the variation in amygdular mineral content (Table 2), and their unweighted average is shown in column 11. Samples 2S through 4S and 6S through 8S in Table 4 are solely the albite

TABLE 4

ANALYSES OF KEARSARGE AMYGDALOID, KEARSARGE FLOW AND SPILITE

Sample number	2	3	4	5	6	7	8	2S	3S	4S	5S	6S	7S	8S	10	11	12	13
Elements:																		
SiO_2	49.2	42.9	57.0	41.4	55.0	54.2	53.8	50.4	52.4	54.0	38.5	55.8	54.0	54.0	48.55	52.0	53.4	52.94
Al_2O_3	12.8	11.8	11.3	15.8	12.0	12.2	12.8	12.4	12.6	11.8	16.0	11.1	11.3	12.4	16.51	12.2	11.9	12.81
FeO	1.4	0.5	0.73	1.1	1.0	2.4	3.5	0.97	0.64	0.66	1.4	0.86	1.5	2.7	6.53	1.6	1.22	9.29
Fe_2O_3	11.3	9.8	11.6	10.3	12.0	11.6	8.7	12.5	12.5	11.9	8.2	11.8	12.7	9.2	4.36	10.8	11.8	3.76
Total Fe as Fe_2O_3	12.8	10.4	12.4	11.5	13.1	14.2	12.6	13.6	13.2	12.6	9.7	12.8	14.3	12.2	11.54	12.6	13.1	13.97
MgO	5.4	2.4	2.6	3.2	3.6	5.8	7.0	5.4	3.6	3.0	4.2	3.5	4.4	5.8	6.68	4.5	4.3	3.65
CaO	7.4	16.2	8.8	21.1	6.5	3.8	4.3	6.6	6.4	8.3	22.3	6.0	5.2	5.0	9.44	7.8	6.3	6.22
Na_2O	5.8	5.8	4.2	0.40	5.0	5.0	5.0	6.0	6.9	5.5	0.27	5.8	5.9	5.8	2.82	5.1	6.0	5.25
K_2O	0.87	0.08	0.06	0.05	0.48	0.78	0.16	0.22	0.05	0.03	0.01	0.10	0.27	0.15	0.58	0.41	0.14	0.18
TiO_2	1.6	1.3	1.6	1.6	1.7	1.6	1.8	1.9	1.8	2.0	1.8	2.0	1.9	2.1	1.49	1.6	2.0	2.54
P_2O_5	0.27	0.22	0.27	0.23	0.24	0.26	0.30	0.30	0.28	0.36	0.27	0.32	0.32	0.35	0.18	0.26	0.32	0.36
MnO	0.16	0.14	0.15	0.22	0.14	0.16	0.19	0.15	0.12	0.16	0.20	0.12	0.14	0.16	0.16	0.16	0.14	0.21
CO_2	1.4	7.2	<0.05	<0.05	<0.05	<0.05	<0.05								0.15	2.5		nil
H_2O	2.6	1.4	1.7	4.5	1.9	2.4	3.7									2.3		
H_2O+															2.06			
H_2O-															0.63			
Loss, on ignition								3.0	2.8	2.4	6.4	2.1	2.3	2.4			2.5	
Cu								0.16	0.055	0.022	0.0028	0.13	0.065	0.061	0.009		0.083	
Sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100				
S.G. (powder)	2.86	2.87	2.91	3.23	2.86	2.86	2.84			2.96	2.78				2.90			
Volume percent amygdules	19	40	15	7	25	33	12	0	0	0	0	0	0	0				

Samples 2 through 8 are of Kearsarge amygdaloid including amygdule filling; samples 2S through 8S are the same specimens with amygdule minerals removed. Location of samples is indicated in Figure 9A. Analysts: Harry F. Phillips, Paul L. D. Elmore, Katrine E. White; Quantitative Spectrographic Analyses of copper by Harry J. Rose. Specific gravity determinations by Paul W. Scott. Column 10 is weighted average Kearsarge flow exclusive of top 12 feet, calculated from Broderick (9, p. 523). Column 11 is unweighted average of analyses of albite basalt with amygdule filling (2 through 4, 6 through 8). Column 12 is unweighted average of albite basalt without amygdule filling (2S through 4S, 6S through 8S). Column 13 is a spilite from Great King Island, New Zealand (4, p. 417).

basalt of the groundmass. Samples 5 and 5S are pumpellyitized rock, the former containing amygdular minerals, and latter representing only the groundmass.

In Table 5 are other analyses of amygdaloidal rock. Sample 9 is pumpellyitized rock with quartz, epidote, and laumontite filling. Sample 1 is an albite basalt with chlorite, microcline, calcite, and pumpellyite filling. Samples from the Iroquois mine, I-1 with prehnite, calcite, and quartz filling; I-2 with laumontite and calcite filling, are similar to the albite basalts of the Kearsarge amygdaloid. Sample 2-36 is a slightly pumpellyitized rock with quartz, epidote, and chlorite amygdules much like the type specimen, except for a slightly greater silica content. Sample 2-24 is a sample of carbonatized

TABLE 5

ANALYSES OF AMYGDALOIDS FROM THE KEARSARGE AND IROQUOIS MINES

Specimen	9	9S	1	1S	I-1	I-1S	I-2	I-2S	2-36	2-36S	2-24	2-24S
Elements:												
SiO_2	52.0	38.4	50.7	50.1	43.3	48.0	43.8	48.6	46.4	43.8	42.9	45.0
Al_2O_3	14.4	15.6	14.2	14.2	15.7	15.1	13.6	14.5	14.2	14.8	12.0	13.4
FeO	0.91	1.8	1.9	1.8	1.8	2.0	3.1	3.4	0.88	1.2	11.2	13.2
Fe_2O_3	9.4	9.8	8.9	9.0	9.4	13.2	8.0	8.7	11.0	8.8	2.6	2.5
Total Fe as Fe_2O_3	10.4	11.8	11.0	11.0	11.4	15.4	11.4	12.4	12.0	10.1	14.9	17.0
MgO	2.2	4.6	7.0	8.9	3.6	4.7	7.7	9.2	4.0	4.6	5.2	6.4
CaO	16.7	20.9	5.6	4.2	14.3	4.6	8.4	3.1	17.2	17.2	10.1	4.9
Na_2O	0.26	0.24	6.0	5.5	4.0	6.1	3.9	5.1	1.4	2.2	0.53	0.06
K_2O	0.04	0.04	0.59	0.49	0.08	0.07	0.79	0.31	0.04	0.05	0.86	0.99
TiO_2	0.90	1.9	1.3	1.2	1.4	1.9	1.3	1.7	1.3	1.4	1.7	2.2
P_2O_5	0.20	0.32	0.16	0.16	0.19	0.26	0.16	0.25	0.23	0.21	0.30	0.38
MnO	0.17	0.20	0.16	0.14	0.11	0.12	0.18	0.20	0.16	0.14	0.12	0.08
CO_2	0.24		0.83		2.7		4.1		<0.05		7.9	
H_2O	2.4		2.9		3.7		5.0		4.2		5.1	
Loss on ignition		5.2		4.2		3.4		4.9		4.9		8.8
Cu		0.0047		0.015		0.0057		0.0060		0.0094		0.065
S.G. (powder)	3.12		2.80	2.73	2.86		2.76		3.12		2.81	2.84

The location of sample 9, from the Kearsarge amygdaloid, is shown in Figure 9B; the location of sample 1 from the base of the flow overlying the Kearsarge amygdaloid, is shown in Figure 9A; I-1 is Iroquois amygdaloid from the 18th level of the Iroquois mine, 130 feet north of the shaft; I-2 is Iroquois amygdaloid from the 19th level of the Iroquois mine, 635 feet north of the shaft; 2-36 is Kearsarge amygdaloid from the 36th level of the Ahmeek mine, 85 feet north of the No. 2 shaft; 2-24 is Kearsarge amygadoloid from the 24th level of the Ahmeek mine, 85 feet north of No. 2 shaft. Samples 9S, 1S, I-1S, I-2S, 2836S and 2-24S are the same samples with all amygdule minerals removed. Analysts: Harry F. Phillips, Paul L. D. Elmore, Katrine E. White, quanitative spectrographic analyses of copper by Harry J. Rose. Specific gravity determinations of Paul W. Scott.

amygdaloid such as that shown in Figure 10D. The table also contains analyses of the same rocks (marked with S) with amygdule minerals removed.

Pumpellyitized rock and albite basalt are known to occur in many of the other mines. Pumpellyitized rock was reported (13) in many mines, and is seen in many dumps and in countless drill cores from both minable and barren amygdaloids. Thin section study and analyses have revealed that albite basalt occurs in the Iroquois amygdaloid (Table 5, column I-1, I-2, I-1S, I-2S), the Osceola amygdaloid, and several other flow tops. Since this rock is not distinguishable from normal basalt in hand specimen, a great deal more microscopic study than was undertaken in this investigation would be required to determine the extent of albite basalt in the Portage Lake lavas.

The composition of the groundmass of the Kearsarge amygdaloid (Table 4, column 12), an albite basalt, is very much like that of an analysis (Table

4, column 13) considered typical of spilites by Verhoogen (51, p. 204), except for the ferric-ferrous iron ratio. This is in contrast to the composition of the Kearsarge flow, exclusive of the amygdaloidal top (Table 4, column 10) which was recalculated from Broderick's analyses, weighted in proportion to the thickness of flow that they represent.

Although spilites have been regarded by some as a primary product of magmatic crystallization, many investigators have suggested that they were formed by replacement of a more calcic plagioclase by albite (51, p. 201–212). A primary origin for the albite basalt of the Kearsarge flow has not been proved, and another reasonable hypothesis is that the amygdule fillings, the pumpellyitized basalt, and the albite might all originate through alteration of basalt.

The texture of the albite basalt indicates that any replacement must have occurred without appreciable volume change by the pseudomorphic replacement of a calcic plagioclase by albite. This suggests some such equation as:

$$CaAl_2Si_2O_8 + Na^+Si^{4+} = NaAlSi_3O_8 + Ca^{++} + Al^{3+}$$

This equation indicates that of every gram of Na_2O introduced (as recorded in an analysis of the rock), 1.94 grams of SiO_2 have been added and 1.81 grams of CaO and 1.65 grams of Al_2O_3 removed. Eskola, Vuoristo, and Rankama (27) have shown experimentally that at temperatures in the range 260° C to 330° C, and confining pressure in the vicinity of 220 atmospheres, anorthite readily reacts with sodium carbonate solution and silica in a closed system to give the assemblage albite-calcite. Oligoclase and andesine develop above 360° C. As noted above, the temperature of formation of calcite and quartz is in the range from 133° C to 360° C. That this reaction may well have been the process by which albite formed in the albite basalt of the Kearsarge flow top is indicated by the calculation in Table 6. Turner (50, p. 122) has made a similar calculation in his discussion of spilite origin. Sufficient soda is subtracted (column 2) from the analysis of average albite basalt from the Kearsarge flow top (column 1) so that soda is equal to the soda of the average basalt of the Kearsarge flow (column 5). Silica is subtracted from and calcium oxide and alumina added to the albite basalt in appropriate amounts relative to soda as required by the equation above. Turner has pointed out if the percent of CaO, Al_2O_3, and SiO_2 resulting from such recalculation (column 4) is not unlike the percent of these constituents in the analysis of the basalt before alteration (column 5), the albite basalt (spilite) may possibly have been formed by replacement of primary basalt. The close similarity of columns 4 and 5 of Table 6 supports the conclusion that the original top of the Kearsarge flow very possibly had about the same chemical composition as the interior of the flow, and that the spilite is a result of alteration involving addition of soda and silica.

Analyses f the Kearsarge flow, of the average albite basalt in the groundmass of the Kearsarge amygdaloid, and of the pumpellyitized groundmass (represented only by sample 5S in Table 4) are converted to grams per 100 cc in Table 7 by taking account of the specific gravity. The specific gravity

of all the albite basalt specimens was not known, but the figure chosen for the calculation, 2.85, is reasonable. More detailed consideration of the albitization process suggested above is now permitted. A comparison is made of gains and losses of all of the constituents during a process of volume for volume transformation of basalt of the composition of the average of the Kearsarge flow into albite basalt of the composition now found in the Kearsarge mines. As shown in column 4 of Table 7, soda, silica, and some iron oxide would have to be added and calcium, aluminum, magnesium, and potassium oxides are lost.

That pumpellyitized rock is also formed by volume for volume replacement is indicated by the microtexture of this rock in thin section. Pumpellyite is pseudomorphous after the feldspar laths. Gains and losses in the alteration of 100 cc of the average Kearsarge flow to 100 cc of pumpellyitized

TABLE 6

COMPARISON OF KEARSARGE FLOW TOP WITH HYPOTHETICAL FLOW TOP BEFORE ALBITIZATION AND WITH THE AVERAGE KEARSARGE FLOW

	(1)	(2)	(3)	(4)	(5)
SiO_2	53.4	−6.20	47.2	46.4	48.5
Al_2O_3	11.9	+5.28	17.2	16.9	16.5
CaO	6.3	+5.79	12.1	11.9	9.4
Na_2O	6.0	−3.2	2.8	2.8	2.8
Remainder	22.8		22.4	22.0	22.8
Total	100.0		101.7	100.0	110.0

(1) Groundmass of average albite basalt of the Kearsarge amygdaloid (col. 12, Table 4).

(2) Amount to be added or subtracted from (1) to yield same percent soda as average Kearsarge flow (5), as required by equation $2CaAl_2Si_2O_8 + Na_2O + 2SiO_2 \rightarrow 2NaAlSi_2O_8 + 2CaO + Al_2O_3$.

(3) Resultant weights in the same volume of the assumed parent rock of the Kearsarge flow top, before albitization.

(4) (3) recalculated to 100 percent. (Hypothetical flow top before albitization).

(5) Average Kearsarge flow exclusive of flow top, calculated from analyses in Broderick (9, p. 523).

rock are shown in column 5 (Table 7). Calcium oxide, water, and CO_2 (included here in "Ignition") have been added and all other oxides of all other major constituents, Na, K, Al, Mg, and Fe have decreased in amount. The large losses of silica and soda are notable. Epidotization may produce the same gains and losses, since the composition of epidote and pumpellyite are very similar, but we have no data on this process.

That the pumpellyitization, albitization, and vesicle filling were the results of a single hydrothermal introduction is suggested by the complementary nature of the chemicals added and subtracted during the two alteration processes. The chemical changes are illustrated diagrammatically in Figure 10. The loss of soda and silica during pumpellyitization is complementary to the gain in these constituents during albitization. Calcium is provided by albitization and needed for pumpellyitization but the calcium needed for pumpellyitization, as explained below, may be derived entirely from the postulated

TABLE 7

GAINS AND LOSSES DUE TO ALTERATION OF THE KEARSARGE FLOW, EXPRESSED IN GRAMS PER 100 CC OF ROCK

	Average Kearsarge flow except top 12 feet	Average albite basalt of Kearsarge amygdaloid (2S–4S 6S–8S)	Pumpellyitized groundmass of Kearsarge amygdaloid (5S)	Gain and loss due to albitization of groundmass (column 2 − column 1)		Gain and loss due to pumpellyitization of groundmass (column 3 − column 1)		Chemicals freed and deficient due to alteration of Kearsarge flow producing 100 cc of albite basalt and 122 cc of pumpellyitized rock (1.22 × column 5 + column 4)		Equivalent mols of freed materials $\left(\frac{\text{column 6} \times 10}{\text{Molecular weight}}\right)$	Gain and loss due to pumpellyitization of albite basalt top (column 3 − column 2)	
Column.....	1	2	3	4		5		6		7	8	
Specific gravity....	2.90	2.85	2.78	Gain	Loss	Gain	Gain	Deficient	Freed		Gain	Loss
Elements:												
SiO_2	140.9	152.2	107.0	11.3			33.9		30.1	5.01		45.2
Al_2O_3	47.9	33.9	44.5		14.0		2.4		16.9	1.65	10.6	
FeO	18.9	3.5	3.9									
Fe_2O_3	12.8	33.6	22.8									
Total Fe as Fe_2O_3									(3.9 as FeO)	(0.54 as FeO)		
	33.6	37.3	27.0	3.7			6.6		4.3	0.27		10.3
MgO	19.4	12.3	11.7		7.1		7.7		16.5	4.09		0.6
CaO	27.3	18.0	62.0		9.3	34.7		33.0			44.0	
Na_2O	8.1	17.1	0.75	9.0			7.35	0				16.35
K_2O	1.68	0.39	0.03		1.29		1.65		3.30	0.35	0.36	
TiO_2	4.3	5.7	5.0	1.4		0.7		2.2				0.7
P_2O_5	0.52	0.91	0.75	0.39		0.23		0.67				0.16
MnO	0.46	0.40	0.56		0.06	0.10		0.06			0.16	
Loss on ignition		7.1	17.8		1.1	9.6		10.6			10.7	
CO_2	0.44											
H_2O	7.8											
Cu	0.026	0.236	0.0078	0.210			0.018	0.188				0.228
Total grams of components freed (SiO_2, Al_2O_3, total Fe as Fe_2O_3, MgO, K_2O)									71.1			

TABLE 8

MOLECULAR RATIOS OF SiO_2 TO Al_2O_3 CALCULATED FROM COMPOSITION OF MORE COMMON AMYGDULE MINERALS AND FROM COLUMN 7, TABLE 7

Minerals	Composition	Molecular ratio SiO_2/Al_2O_3
Laumontite	$CaAl_2Si_4O_{12}4H_2O$	4 to 1
Prehnite	$Ca_2Al_{0.2}Fe^{+++}_{0.2}AlSi_3O_{10}(OH)_2$	About 3.5 to 1
Epidote	$Ca_2Al_{2.2}Fe^{+++}_{0.8}Si_3O_{12}(OH)$	About 2.5 to 1
Chlorite	$(Mg_{2.1-2.8}Fe^{++}_{2.8-2.1}Al_{0.4})_6(Si_{2.8}Al_{0.4})_4O_{10}(OH)_8$	About 9 to 1
Microcline	$KAlSi_3O_8$	6 to 1
Calculated from column 7 of Table 7		3.0 to 1

hydrothermal solutions and the calcium released from albitization be used entirely to form the calcium amygdule minerals. In each type of alteration the losses from the original rock in excess over those needed for the complementary alteration may be postulated to have made up the required material for the amygdule fillings. Pumpellyitization alone would supply silica but not enough alumina (column 5, Table 7) for the aluminous minerals prehnite, microcline, and epidote. On the other hand albitization would not supply any silica but would supply alumina (column 4, Table 7) for these minerals. Only pumpellyitization supplies silica for quartz. Since neither type of alteration supplies carbon dioxide for calcite, and calcium in excess of that

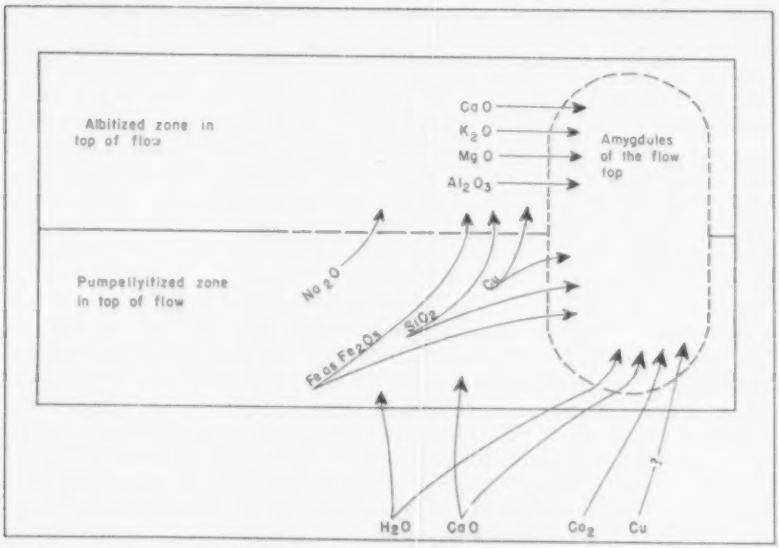

FIG. 10. Direction of chemical changes during alteration of the top of the Kearsarge flow shown diagrammatically. (Based on figures of Table 7.)

supplied by albitization is required to satisfy the requirements of the pumpellyitized rock, the introduction of carbon dioxide as well as calcium and water must be postulated.

Geologic evidence favoring the hypothesis that the amygdule fillings are related to pumpellyitization is provided by the close association of quartz in amygdules in the pumpellyitized groundmass and its diminution at a distance from this type of alteration in individual flow tops. This is a relationship to be expected as a result of the large amount of silica freed by pumpellyite alteration. The prevalence of this type of alteration in, rather than outside, the quartz zone, as described in the section on regional zoning, is compatible with the hypothesis that this type of alteration provides silica and other chemicals for vesicle filling. Relationships between albitization and vesicle filling are not readily discernible in the field. The albite of the lavas is apparently fresh and partial replacement of calcic plagioclase by albite has not been noted in thin section. That the prehnite, chlorite, or epidote of adjacent basalts is related to albitization of spilites has been noted by Turner (50, p. 124). However, Turner's emphasis in this reference is on the formation of these minerals due to the lime set free during albitization rather than on the complementary nature of the sequential processes of pumpellyitization, albitization and vesicle filling that we suggest.

It is difficult to analyze quantitatively the role of chemicals released during alteration in relation to the composition of the amygdules. This is chiefly because one cannot estimate with any assurance the average total composition of the amygdules of the Portage Lake lavas or even of any part of the series such as a particular flow. How far the released products may have travelled before depositing in the interfragmental spaces and vesicles is unknown and there is no reason to believe that all constituents would have travelled equal distances before precipitation. If pumpellyitization was the source of the soda needed to albitize the Kearsarge flow it is clear from the calculated losses and gains during these processes in the Kearsarge amygdaloid (columns 4 and 5 and Table 7) that enough soda will be released to albitize one volume of flow top only if 1.22 volumes of flow top are pumpellyitized (9.0 grams of soda is gained in 100 cc albitized rock; 7.35 grams of soda is released in pumpellyitizing 100 cc of rock, so 9.0 grams of soda are released in pumpellyitizing 122 cc of rocks; $7.35/100 = 9.0/122$). Since amygdule minerals are low in soda this is not only a minimum figure but also probably not far from a maximum. Therefore, assuming the alteration involves a ratio of 100 cc of albitized rock to 122 cc of pumpellyitized rock, the total iron, silica, alumina, magnesia and potassium oxide released for amygdule filling may be calculated. These figures are shown in column 6 of Table 7. The amount released from a total of 624 grams of rock (100 cc, or 285 grams, of albite basalt plus 122 cc, or 339 grams, of pumpellyitized rock) is 71.1 grams or about 11.4 grams per 100 grams of altered material. This is the order of magnitude to be expected. The volume percent of vesicle filling in the Kearsarge flow ranges from about 5 to 30 percent of the volume of the rock (Tables 2, 4).

The calculated analysis of the released material (column 6, Table 7) is converted to equivalent mols in column 7 of Table 7. The mol ratio of

silica to alumina is 3.0 to 1. The molecular ratios of SiO_2 to Al_2O_3 in the common minerals of the amygdule fillings are shown in Table 8. The silica alumina ratio of the amygdule minerals all taken together must surely equal or (due to quartz) somewhat exceed the ratio calculated for the material freed by pumpellyitization and albitization.

The amount of magnesia in column 7 Table 7 suggests that some of the chlorites must be higher in magnesia than the chlorite of the Kearsarge for which optical data is available. There is also the possibility that the chemical composition cited for the chlorite (Table 8) is higher in iron and aluminum than is really the case. Our meager knowledge of the relationship between optical properties and chemical composition of chlorites make this a distinct possibility. The potash content is surely sufficient and may be more than enough to account for the not-too-abundant microcline. A more quantitative extrapolation seems unwise with present data.

One may conclude that if soda is supplied by pumpellyitization for the albitization, the volume of rock pumpellyitized must be a little greater than the volume of albitized rock and the elements thus freed may be in appropriate proportion so that with the addition of calcium oxide and carbon dioxide they could form the minerals that actually fill the vesicles of the lavas. If this conclusion is accepted, there has been a transfer of material into the part of the Kearsarge amygdaloid that has been studied, for the pumpellyitized rock makes up one quarter or less of the total flow top in any average cross-section. Pumpellyitized rock is rare above the quartz zone in the upper levels (Fig. 8) and is common in the deep levels. A transfer of material from down the dip rather than a chemical rearrangement in situ is clearly indicated. Inclusion studies showing that quartz at depth was deposited at higher temperatures than near the surface leads to the same suggestion, through the assumption that the amygdule minerals were deposited by hydrothermal solution that cooled as they traveled up dip from their source.

It has been tacitly assumed that the pumpellyitized rock is formed by replacement of a flow top with composition like that of the average Kearsarge flow excluding the flow top. As noted above, others believe that albitization of the flow top was deuteric and therefore earlier than the pumpellyitization. If one considers the flow to have been albite basalt before pumpellyitization the elements gained and lost during alteration are in marked contrast to the calcium oxide and water assumed necessary under the complementary pumpellyitization-albitization-vesicle filling hypothesis presented above. If the flow top was albitized before and independent of pumpellyitization, the alteration to pumpellyite would not have provided appropriate chemicals for amygdule filling. Column 8 of Table 7 shows that calcium oxide, alumina, potash and water would all be required for pumpellyitization of albite basalt; silica, soda, some iron and a little magnesia would be lost. The amounts of silica and calcium oxide involved are large. Very little soda is found in amygdule filling minerals and potash and alumina as well as calcium and water would have to be added. Though the soda could be carried away and the other required elements may have been added the process is much more complicated than the one outlined above.

As an alternative one might assume that both pumpellyitization and albitization were deuteric in origin. Freed elements then would be distributed later by hydrothermal waters. This hypothesis is untenable. Pumpellyitization is spatially related to the quartz vesicle filling both in detail, as in the Kearsarge and other amygdaloids, and areally. The vesicle filling and related rock alteration is later than tilting of the flows, for the mineral zone boundaries cross stratigraphic boundaries. Clearly, pumpellyitization is not deuteric, and if albitization is part of the same exchange of materials, it, likewise, is not deuteric.

The discussion has thus far emphasized the major constituents. Their magnitude is in general large enough to make sampling and analytical errors insignificant. It is probably also safe to assume, as we have, that the amount of each major constituent in the flow top and in the flow as a whole were originally almost the same. It is, however, quite likely that the abundance of minor constituents in the Kearsarge flow top may have differed from their abundance in the average for the flow, which has been used for the calculations presented here. As noted above, volatile transfer during the formation of the flow has been postulated by earlier writers. All of the minor constituents do not fit into the hypothesis outlined here; for example, the oxides of phosphorus and titanium are gained during both alteration processes (columns 4 and 5, Table 7), as is the oxygen needed to form ferric from ferrous oxide. No other constituent except water shows this relationship. Must it be concluded that these constituents were added with water, calcium and carbon dioxide? It seems more likely, following Broderick (9) that the original flow top was enriched in oxygen, titanium, and phosphorus by volatile transfer during the formation of the flow. One might also account in this way for the slight increase in manganese in the pumpellyitized rock.

Copper, in contrast to oxygen, titanium, manganese, and phosphorus, is similar to many of the major constituents in that it is lost during pumpellyitization. This is shown by two analyses of pumpellyitized rock (5S of Table 4; 9S of Table 5) in which copper is 0.0028 and 0.0047 percent, respectively. The original copper in the Kearsarge flow top may have been 0.009 percent, the average for the main body of the flow (column 10, Table 4), or may have been larger due to volatile transfer. Cornwall (16, p. 198–199) has suggested a range from 0.002 percent to 0.04 percent original copper in the lavas of the Portage Lake series, based on the copper content of fine-grained flows in the area; he points out that if, as an extreme, all the copper that has been mined from the Kearsarge amygdaloid were assumed to have been derived from the vertical column of lava beneath it, the original copper content of the lava would be of the order of 0.043 percent. Whatever the actual figures, the available data indicate a loss of copper in pumpellyitized rock.

This is of considerable interest for it provides a suggestion as to the mechanism by which copper might become freed from the flows to be concentrated by hydrothermal solutions in some other part of the flow or a porous conglomerate further up the dip. This mechanism has been discussed

by both Broderick (10) and Cornwall (16, 22) on the assumption that all the copper from the flow top or from the entire flow was removed in the area or areas of release. Whether copper has been gained or lost in the albitized portion of the flow tops is not certain. The minimum copper content in the seven analyses of albitized rock is 0.015 percent. This is more than that in the original flow (0.009 percent) but less than may have been in the flow top originally (up to 0.043 percent). The average value of copper in the albitized rocks, 0.083 percent, is large and may reflect contamination with hydrothermally introduced copper. The data suggest to the authors that copper has been added, at least in small amount.

The new information indicates that there is surely leaching of copper in areas of pumpellyitization. Epidotization may produce the same result, for the two processes seem to go hand in hand in many places, and both minerals are very similar, but we have no data on this process. The leaching of copper may be restricted to areas of such alteration.

Conclusions as to the Origin of the Copper

For the several reasons developed in earlier parts of this paper, copper appears to be one of the several minerals formed due to regional hydrothermal alteration of basaltic lava flows. Evidence presented indicates that the amygdule minerals associated with the copper were deposited by solutions travelling up the dip of tilted lava flows at temperatures probably greater than the values, not corrected for pressure, of 133°–360° C found from inclusion thermometric studies. Many of the chemical constituents of the amygdule minerals came from the flows themselves. We are inclined to believe that the copper did also. Specifically, as suggested in the previous section, the copper may be freed from basalts altered to pumpellyite. It is quite reasonable that this freed copper could be carried up the dip of structurally favorable porous flow tops and deposited near or slightly beyond the limits of pumpellyitized rock. This would be approximately the outer limit of the regional quartz zone, for as noted above, pumpellyitization is limited to areas within the regional quartz and epidote zones. The coincidence of copper with the outer margins of the quartz zone is therefore reasonable. Whether the process of freeing copper by pumpellyitization is quantitatively possible remains a problem that hinges on the locus of alteration. If, at depth, pumpellyitization pervades the whole thickness of the flow enough copper might be freed to provide that now found in the mines. If the alteration is limited to the flow tops as it largely is in the rocks now visible in the district, the process may require a very large source area down the dip. Observation at the depths penetrated by mines suggests that alteration is more extensive throughout the whole flow top at depth, but its extension into the massive basalt underlying the flow top is not established; at greater depths this may well occur.

An alternate hypothesis proposes that the copper was derived from a magma at depth. There are two reasons, which are derived from informa-

tion in this paper, neither of them compelling, for favoring the metamorphic rather than magmatic source. If one accepts the suggestion that the copper distribution is areally related to the regional hydrothermal metamorphic zones marked by amygdule minerals, then, because a regional hydrothermal metamorphic process is adequate to produce the amygdule minerals, one is inclined to believe it may have also produced the areally related copper. The second reason for favoring a metamorphic origin for copper is that the wide area of metamorphism, the entire Lake Superior basin, throughout which there are very small copper deposits, seems to demand a magmatic source of extremely large areal extent, larger than one would like to postulate. In addition to these features, we are impressed with the lack of sulfur in the ores. As suggested by Cornwall (16, p. 197, 20) native copper would more likely result from the metamorphism of relatively sulfur-free copper-bearing lavas than from magmatic emanations, for these latter appear always to contain sulfur.

It is clear to us that the data of the present paper do not preclude a magmatic origin for the copper. McKinstry's comment in a review of papers by Cornwall (41, p. 659) is pertinent: "to prove that the ore *could* have come from the flows is one thing and to prove that it *did* is another." Remarks of a similar nature are presented by Broderick (11, p. 285–287). The present paper, however, attempts to go beyond the observation by Lindgren (39, p. 517) who wrote that the conclusion that copper was extracted from the flows forces itself on the observer. We suggest the mechanism by which copper would be freed from basaltic lavas and point out the regional hydrothermal origin of a mineral pattern of which copper appears to be a part. This simply opens the way for continued speculation as to a possible source of copper by a process of hydrothermal metamorphic regional differentiation, or perhaps one should term the process, following McKinstry (41, p. 659), "a modified form of lateral secretion."

Speculation might take the following form. The cause of the activation by hydrothermal metamorphism on a regional scale of the necessary calcium- and carbonate-bearing waters might have been the downwarping of the lava-filled basin into the hotter deeper regions of the crust. Where the lavas dip steeply, it may be presumed that their down-dip portions are deeper in the earth than where the lavas dip gently; it is not surprising, therefore, that in the zonal relationship now exposed, the steeper dipping flows of the Portage Lake lava series generally carry the higher temperature minerals. The calcium- and carbonate-bearing waters thus activated would have altered the rocks, freeing by this process the several elements. Of these soda would have formed albite from preexisting calcic plagioclase in the basalts, and silica freed from the deep alteration would have aided in the formation of albite. The excess silica would have been deposited in fragmental spaces and amygdules either as quartz or combined with other elements to form potassium, calcium, and aluminum silicates, up-dip from the deeply altered lavas. The copper freed at depth appears to have been carried in large quantities only where there were through-going structural channelways in which,

at the approximate margins of the quartz zone, within the epidote zone, concentrations of native copper were formed.

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THE GEOLOGY OF TORBRIT SILVER MINE

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ABSTRACT

Torbrit Mine, which in 1956 was the third largest silver producer in Canada, is located along the upper portion of the Kitsault River in the Portland Canal area of British Columbia. In the Upper Kitsault River area the Hazelton group of rocks of Jurassic (?) age consist of four formations: Lower Sedimentary, Lower Volcanic, Upper Sedimentary and Upper Volcanic. The rocks form a syncline that plunges at 30° NW. The Hazelton group was intruded by feldspar porphyry in the late Cretaceous (?) and the entire assemblage was cut by andesite dikes in Tertiary (?) time.

The Torbrit orebody occurs in the Lower Volcanic formation. It is a pod-shaped body plunging 30° NW and lies on the northeast end of a vein sheet that strikes N 50° E and dips 45° NW and occupies a tension fracture; the orebody was formed in a horsetail-type shear zone. The gangue minerals are quartz and barite with jasper, calcite and siderite. The main economic minerals are galena, tetrahedrite, pyrargyrite, argentite and silver, with variable quantities of pyrite, chalcopyrite, sphalerite, magnetite and hematite.

By X-ray fluorescence methods the Sr content of eleven barite samples from crustiform layers of Torbrit ore was found to vary from 0.52 to 1.05 percent. The distribution of Sr between solution and barite crystals for 83° C is such that the Sr/Ba ratio is much higher in the crystallizing solution than in the resulting crystals. The variation in the Sr content of the barite in this case is thought to be due to variation of the Sr/Ba ratio in the solution, rather than to temperature variations during formation.

Five sphalerite samples were analyzed for FeS, CdS and MnS by X-ray fluorescence. The averages in weight percent were 0.72 ± 0.2 CdS, 0.19 ± 0.1 MnS, 2.0 ± 0.2 FeS.

A temperature of 270° C was determined for the sphalerite by plotting the FeS content of the sphalerite on a portion of the system ZnS-FeS-S, and by employing the argentite-silver assemblage as a sulfur barometer. This is based on the qualified assumption that sphalerite, pyrite, argentite and silver were formed under equilibrium conditions. Even with the above assumption, the uncertainties of the data indicate the temperature of sphalerite formation could range between 230° and 310° C. The deposit formed at about 300 atmospheres hydrostatic pressure and therefore a small additional correction is necessary.

The orebody was formed in late Cretaceous to early Tertiary, from solutions genetically related to the last phase of the Coast Range intrusion in the area.

INTRODUCTION

Torbrit Silver Mine is located on the Kitsault River 17 miles upstream from Alice Arm in the Portland Canal area of British Columbia (Fig. 1). Alice Arm village lies 115 miles north of Prince Rupert, the largest city and principal seaport in the area. Coastal steamers and seaplanes out of Prince Rupert service the mine via Alice Arm wharf. The minesite, connected to Alice Arm by a 17 mile road, is located along a canyon of the Kitsault River in an extremely steep-walled valley, at an elevation of slightly over 1,000 feet.

History and Production.—In 1916 the Toric claim, which encompasses most of the Torbrit Mine, was staked by the Strombeck brothers of Alice Arm. This claim was optioned by the Consolidated Homestake Mining and Development Co. in 1924. In 1927 the company name was changed to Toric. In 1929 Britannia Mining and Smelting Co. acquired the mine and formed the Torbrit Mining Company, but due to low silver prices the mine was inactive from 1930 to 1949. In 1946 the Mining Corporation of Canada took over the property and began production in 1949.

The estimated average grade of ore treated through the 1949–1957 period was 17.2 oz. Ag and 0.42% Pb per ton. Up to 1957 1,099,798 tons of ore had been milled producing 15,983,652 ounces of silver and 7,857,715 pounds of lead. In 1957 United Keno, Sullivan, and Torbrit ranked in that order in silver production in Canada (13).

The 420-ton mill consists of a crushing plant, flotation circuit, and cyanidation circuit. Eighty percent of the silver is recovered as flotation concentrate; twenty percent as bullion.

It is peculiar, and may have genetic implications, that of ten silver producers in the Portland Canal and Hazelton-Smithers areas, Torbrit and the adjacent Dolly Varden are the only two that have produced no gold (1).

The gold–silver ratio at Torbrit is less than 1 : 100, and is difficult to account for if this ore is to be genetically related to the same coast range intrusives that sired the many gold-bearing deposits in the region. The variation of the gold–silver ratio in deposits of the western United States has been discussed by Nolan (34), but he reached no conclusion concerning either physical or chemical control.

Geological Work.—Since early in the century Alice Arm district and later the Kitsault River area have been investigated geologically. In 1917 Turnball (40) discussed the geology and mineral deposits of the Alice Arm district, but Hanson (18, 19, 20, 21, 22, 23, 24) has been by far the larges. contributor to the knowledge of the geology of the region. His cumulative works cover a strip from Stewart, B. C., to the Skeena River and give an

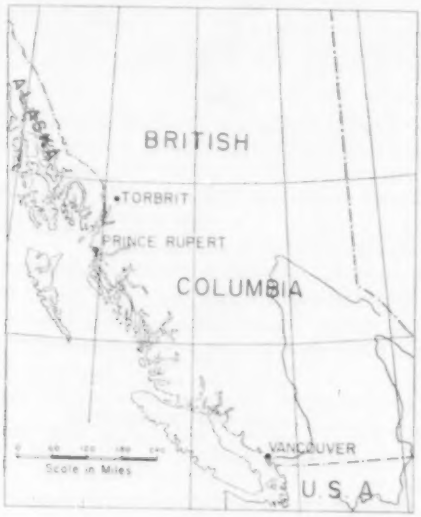


FIG. 1.

excellent regional perspective. Armstrong (1), as the result of many studies in northern British Columbia, gives a fine discussion of the stratigraphy, structure, geologic history, and ore deposits of this region. Black (3), in 1951, made a study of the Upper Kitsault River and his work is specific and pertinent to the present discussion. The work of all these men plus the writer's work of two field seasons at Torbrit mine are used in the interpretation of the geology of the Upper Kitsault River.

Acknowledgments.—I wish to thank Torbrit Silver Mines Ltd. for the opportunity of making this study.

The laboratory work for the study was carried out at Princeton University, and was greatly facilitated by the available equipment and helpful suggestions of both the faculty and students. I am particularly grateful to

Dr. Sampson and Dr. Kalliokoski for guidance in the study, and for critically reading the manuscript. Dr. Holland was very stimulating and helpful in discussions of the geochemical aspects of the investigation, as well as in making calculations. I wish to acknowledge the financial assistance of a research assistantship, and the Canadian Alumni Fellowship, while at Princeton University.

I am grateful to Dr. Paul B. Barton Jr. of the United States Geological Survey, who very kindly supplied data for part of the ZnS-FeS-S system. Dr. J. A. Jeletzky, of the Geological Survey of Canada, identified fossils collected in the area.

GEOLOGY OF THE UPPER KITSAULT RIVER

The rocks in the Upper Kitsault River area form a syncline that strikes slightly west of north and plunges 30° N. Folding has involved four formations of the Hazelton group, two sedimentary and two volcanic. This sequence has been intruded by feldspar porphyry, and later by a series of andesite dikes of possible Tertiary age.

TABLE 1

TABLE OF FORMATIONS OF THE UPPER KITSAULT

Tertiary (?)		Andesite dikes
		—Intrusive contact—
Cretaceous (?)		Feldspar porphyry
		—Intrusive contact—
Jurassic (?)	Hazelton group	Upper Volcanic formation Volcanic breccia and tuff, locally graywacke and shale
		Upper Sedimentary formation Shale, argillite, graywacke, tuff
		—Local unconformity—
		Lower Volcanic formation Propylitized volcanic breccia tuff, and andesite
		Lower Sedimentary formation Argillites with interbedded graywacke, local conglomerate

Hazelton Group.—The Hazelton group, which is the country rock of the area, is a heterogeneous assemblage of volcanic breccias, tuffs, and flows with poorly differentiated sediments. These are products of vulcanism and sedimentation in an unstable paralic environment, and as such show much wedging of units and intermixing of material. The four formations of the Hazelton group used in this study cannot be correlated with rock units of the same group in other areas. Their extent beyond the map area of the upper Kitsault is unknown.

The division of the group into formations is based on gross lithologic aspect and the formations used are those introduced by Black (3). Stratification, marine fossils, and weathered clastic components were used as the distinguishing criteria for sedimentary rocks. Arbitrary limits were set in the field as there is much intermixing of volcanic and sedimentary units.

In general the pyroclastic rocks with which we are dealing are the normal products of explosive vulcanism when large quantities of pyroclastic material was produced and rapidly deposited. I feel that the amount of reworking of this material is undeterminable because all primary material and structures have been modified by the pervasive alteration. Some mud sliding is suggested by the shape and distribution of some members of the lower volcanic formation, but even this cannot be proved.

The sedimentary formations indicate times of more normal sedimentation as shown by the stratification, bedding and marine fossils. In the upper Kitsault region, the fossils are generally more abundant in the greywacke members. This suggests an increased death rate in this undoubtedly more turbid depositional environment. Indeed, the general paucity of fossils in the Hazelton group indicates that their site of formation was unfavorable for the sustained existence of life.

The exact time limits of this group and its stratigraphic correlation throughout central British Columbia has been a problem concerning geologists of this area for some time. (11, 29, 32, 27, 22, 24), mainly because of the lack of diagnostic fossils, and the rapid changes in lithology.

During the present work a few fossils were collected on the Moose and Tiger claims as well as near the mouth of Wolf Creek and these were submitted to J. A. Jeletzky of the Geological Survey of Canada who thinks the fauna indicate a probable Jurassic Age.

Feldspar Porphyry.—An autobrecciated body of feldspar porphyry, having the composition of rhyodacite, has intruded the Hazelton group. The rock contains plagioclase in the oligoclase range, no potash feldspar, and over 10 percent quartz. It is in all places altered and those parts that are most strongly altered and intensely pyritized have been given the confusing name of "Copper Belt" intrusive.

The most evident feature of this intrusion is the red and yellow iron oxide staining that is produced by the weathering of small quantities of pyrite. Consequently this conspicuous rusty ridge along the west side of Kitsault River has attracted prospectors since the early days of this century. However, the staining is only a fraction of an inch deep and beneath this the rock exhibits its light grey color and waxy luster. Although most of the feldspar porphyry tends to be structureless, on some weathered exposures and more rarely on some fresh surfaces the rock exhibits a flow-breccia fabric. The fragments of fine-grained feldspar porphyry, commonly on the order of one to two inches across, are set in a flow-banded aphanitic matrix. The fragments are not visible on all outcrops, possibly because of original absence or the more intense local hydrothermal alteration. Quartz stringers cut the rock and show a marked increase in the more highly altered phases.

A thin section study confirms the highly altered condition of the rock. It appears to have been originally an oligoclase porphyry with laths of zoned feldspar up to 1 mm by 5 mm making up about 50 percent of the rock. Staining indicates that potash feldspar is absent. There is no fluidal arrangement of the feldspars. The aphanitic groundmass is completely altered to sericite, chlorite, and carbonate. Within the groundmass are irregular amyg-

dules, composed of chlorite fillings and quartz rims. In section they always have the shape of collapsed loops and are thus interpreted as original vesicular openings that underwent distortion before filling took place. The presence of amygdules indicates a shallow depth of emplacement for the body.

From the evidence it seems that the intrusion underwent autobrecciation during emplacement at a shallow depth, so that the fabric is one in which feldspar porphyry fragments are separated by narrow zones and seams of aphanitic material of the same parentage. The entire rock has since been silicified, carbonatized, chloritized, and pyritized to such an extent that the breccia fabric is difficult to see except on a few outcrops or on polished specimens.

The introduced pyrite is present in varying proportions throughout the rock, but the greatest concentration is in the "Copper Belt" phase, near the eastern margin of the intrusion, where pyrite commonly forms pods and veins. The locus of numerous copper occurrences is also along the eastern margin of the feldspar porphyry body, coincident for the most part with the limits of the "Copper Belt" phase. The copper mineralization has been accompanied by superimposed chloritization, thus imparting various shades of green to the rocks. The chalcopyrite mineralization is cut by quartz-barite veins, and both are cut by andesite dikes.

The intrusion was controlled somehow by the axial plane of the syncline. It rose along a fracture in the Lower Sedimentary and Volcanic formations and then spread out in a sill-like fashion between the lower volcanics and the overlying sediments. Judging by the larger exposures of the rock, the ease of intrusion to the west of the axial plane must have been greater than to the east. However, smaller bodies do occur to the east of the axial region on the Ouray claim and at the headwaters of Tiger Creek, so that the body does possess some symmetry.

The feldspar porphyry was broken by a series of northeast trending, steeply dipping, normal faults with the relative movement of each fault being north side down. The widths of the porphyry varies from 1,000 feet in the most southerly block to over 3,000 feet in the most northerly block. This pattern of increased width going northward in the successive fault blocks suggests that the porphyry intrusion has a fissure root that flares out at higher elevations. Furthermore, the porphyry body may have a northerly plunge similar to that of the principal syncline as suggested by the fact that the intrusive does not appear south of the most southerly fault. Because the east contact of the intrusive shows no great displacement at the faults, this has been interpreted as indicating a steep dip on the east side. This easterly margin is much pyritized and is hence believed to lie above the main fracture and feeder for the intrusion.

Hydrothermal Veins.—Numerous mineral showings occur in the valley of the Upper Kitsault, that may be broadly classed as gold-bearing and non-gold-bearing.

The gold-bearing deposits are steeply dipping veins mainly in the "Copper Belt" phase of the feldspar porphyry intrusive and occur near or along its eastern margin. The veins occur in silicified and chloritized shear zones, and contain pyrite, and chalcopyrite, with minor sphalerite and galena. They

also carry variable quantities of gold with minor silver. Examination of the deposits in detail, indicates that the shoots of ore within the shears plunge northerly.

The non-gold-bearing veins occur as fissure fillings and replacements of quartz, barite, jasper, carbonate, with silver minerals, galena, sphalerite, pyrite and chalcopyrite. No gold values have been recorded from these deposits. These veins are best developed in the Lower Volcanic formation, particularly along the east limb of the syncline. It is significant that quartz-barite veins cut both the porphyry, and a copper and gold-bearing shear zone, thus indicating a younger age for this second class of deposits.

Dikes.—Swarms of andesite dikes trend N 30° E across the area. The two principal groups are seen at Torbrit mine and crossing Black Bear Creek above the Red Point claim. Others undoubtedly are present but can be easily overlooked unless detailed mapping is done. The reason for this is the tendency for the jointed dikes to disintegrate rapidly on weathering as well as the general lack of good exposures in the area. The dikes cut all other rocks and veins and may represent Tertiary lava feeders.

Structural Geology of Upper Kitsault Area.—The rocks of the Upper Kitsault are the northern portion of folded Hazelton group rocks that are exposed from Alice Arm to the Kitsault Glacier. At Alice Arm the sequence forms two synclines separated by an anticline. Six miles north of Alice Arm the synclines coalesce and the anticline disappears. In the vicinity of East Creek about three miles south of the mine, and 12 miles north of Alice Arm, the structure is arched along a northeast axis. North of this axis in the Upper Kitsault region the rocks plunge north at about 30°.

There have been at least two opposed views regarding the structure of the region. Hanson (18) in the first comprehensive study of the area, recognized only one sedimentary and one volcanic sequence, and equated the synclinal sediments in the central part of the area with those to the east and west on the flanks of a major anticline. On the basis of this correlation he made the volcanic sequence older than the sediments, and interpreted the structure as an anticline with a minor central syncline. Black (3), on the other hand, recognized that the upper and lower sedimentary rocks are separate sequences. On the basis of this clarification and on the structural relations between the volcanic and sedimentary rocks in the Upper Kitsault area, he advocated that the main structure was a syncline. I agree with the latter view and find the geology at Torbrit in general to support this interpretation. In detail the structural history of the Upper Kitsault area is still far from being completely understood.

A zone of weakness near the axial plane of the syncline gave ingress to the feldspar porphyry. In a later discussion this will be tentatively related to a structural zone parallel to the margin of the batholith. A peculiar zone of faulting northeast of the Torbrit ore body may be in part related to this regional line of rupture. The latter faults strike northwesterly parallel to the zone of weakness and dip 75° W. They thrust up the flank of the syncline northeast of the orebody and against the wedge of andesite to the northeast. The pile of andesite appears to have had an initial slope of about 15 degrees as it thins both down dip and along strike to the south. The more

competent andesite has impinged on the other rocks during folding and was partly responsible for the fracture pattern that enabled solutions to penentrate the present region of the Torbrit orebody (Fig. 6). The shape of the mass may have caused some left-hand transverse, as well as thrust movement during folding. Exactly how much movement is involved is not known.

A set of northeasterly striking faults and associated joints have so strongly influenced the drainage pattern that the tributary creeks on the west side of the Kitsault River flow northeast, and the streams on the east side conform to the normal pattern and flow to the southwest, whereas the Kitsault flows due south. The above, nearly vertical faults are interpreted to be normal with the north side down. They cannot be part of the strain pattern caused by the compressive stress that resulted in the subsequent folding. If they were, one would expect a right-hand movement or the south side down. Instead, it is believed that this fault set is related to the period of uplift that arched the sequence along an axis some three miles south of the mine. The strike of the faults is approximately parallel to that axis. Because the fault displacements are only evident on the west side of the syncline, I feel that this movement was caused by rotational tilting with the west side of each block having dropped more than the east. The formation of the arch may have taken place in Tertiary time as the joints and normal faults were subsequently filled by Tertiary (?) andesite.

A general summary of the sequence of events in the Upper Kitsault is as follows:

1. Deposition of lower sedimentary and volcanic members of the Hazelton group.
2. Slight uplift and local erosion.
3. Deposition of upper sediments and volcanics.
4. Folding with compression from southwest and northeast began.
5. Intrusion of feldspar porphyry; continued compression through stages 6 and 7.
6. Early fissures intimately associated with "Copper Belt" copper-gold mineralization.
7. Later fissures containing silver-lead deposits, mainly in lower volcanic rocks. Original fractures probably originated in stage 4.
8. Uplift caused arching in vicinity of East Creek, giving north plunge to syncline in Upper Kitsault region and forming NE-striking normal faults. This, in part, contemporaneous with compressive stage.
9. Andesite dikes intruded into dilatant zones of normal faults. Minor post-dike faulting.

GEOLOGY OF TORBRIT MINE

The mine lies entirely within the Lower Volcanic formation near the major synclinal axis. The ore is in shoots in a pod-shaped, chambered body of vein material at the eastern end of a vein sheet. The sheet has a variable strike that approximates N 50° E, a dip near 45° N and the pod plunges 30° NW. The ore has been affected by minor faulting and has been cut by numerous andesite dikes.

The banded, contorted appearance of the vein material and the pod shape suggest several possible origins for the orebody. Replacement of a sequence of favorable beds, or replacement and filling of a tectonic breccia zone or a diatreme-like pipe were all considered as methods of emplacement of the orebody. I feel that the evidence favors replacement and filling of a sheeted and brecciated zone by gangue and ore.

Much of the effort in this study was devoted to dividing the volcanic assemblage that contains the vein material into mappable units, in order to interpret the structures better. As the surface exposures alone are not good enough to guide this type of subdivision, much information was gained from the study of 60,000 feet of diamond drill core, and the mapping of all accessible underground workings at the mine and in the numerous adits along the valley. It was impossible to use aerial photographs in mapping as the forest cover is too heavy for detailed location. For this reason a base map was constructed by running traverses from surveyed departure points using a Brunton compass on a tripod, a clinometer, and a chain. On this basis two men were required for each traverse party to establish the position of each outcrop. A detailed topographic map at a scale of one inch equal to 200 feet, so important for structural control in this rugged terrain, was compiled slowly as mapping proceeded. Further checks on control were afforded by the locations of surveyed claim posts obtained from records of the British Columbia Land Surveys. As an indication of the difficulty of travel in this country, it would take a full day to visit some points less than two miles from the mine. Helicopter transportation was used in the diamond drilling operations along the valley.

Stratigraphy and Lithology

The following table indicates the rock types distinguished in the mine area. It should be made clear that the various members are indicated in

TABLE 2

TABLE OF LITHOLOGIES IN TORBRIT AREA

Period	Group	Formations	Members
Tertiary (?)		Andesite dikes	
		—Intrusive contact—	
Jurassic (?)	Hazelton group	Upper Sedimentary formation	Argillite, graywacke and conglomerate
		—Local unconformity—	
		Lower Volcanic formation	Albite breccia and tufts
			Gray breccia
			Albite andesite
			Purple and green pyroclastic rocks Undifferentiated Bedded tuffs Marker tuffs
		Lower Sedimentary formation	

their chief stratigraphic position and that several of the lithologic types recur as lesser components in other positions.

Vein Material

The vein sheet and pod are composed of variable amounts of quartz, jasper, barite and carbonates. The vein material commonly shows a spectacular crustiform banding with many colloform swirls that are interpreted as indicating colloidal deposition, at least in part, in open spaces. Replacement has played a part in the vein formation, however, as will be shown under a discussion of the wall rock alteration. In places the crustiform and colloform banding has been disturbed by brecciation.

Vein outcrops are not common due to rock slides on the slopes and vegetation on the hilltops. The vein is exposed in trenches on the Dolly Varden claims, and in adits on the Dolly Varden, North Star, Toric, Ruby and Moose claims. Considerable stripping on the Moose claim exposed vein material that follows a discontinuous fracture zone related to the northeastern edge of the Torbrit body proper. Similar vein material carrying variable silver values is found on the Tiger, Muskateer, Wolf, Ouray, Moose II and Climax claims. The present study deals in particular with the Torbrit body and related structures, and the other occurrences are referred to only in connection with the regional setting and metallogenesis.

Structure of the Vein Material.—Contours of the footwall of the vein material indicate that the vein sheet arches into a gentle anticline plunging 40° N as it approaches the Torbrit orebody. In general the footwall of the pod is synclinal, plunging 30° NW. Minor anticlines and synclines occur within the principal syncline. Thus the western portion of the structure is a sheet that strikes N 50° E and dips 45° NW, whereas the eastern portion becomes increasingly complex as the pod-shaped orebody is approached. The general structure of the vein material, much simplified, could be likened to the well known Franklin Furnace syncline, with the difference that the long limb dips almost parallel to the plunge of the trough, and that the major orebody occurs as a thick, elongated pod in the synclinal region. The information on the vein sheet has been derived mainly from diamond drilling as only short adits have penetrated this structure on the North Star claim. For this reason the present interpretation of the regularity of this portion of the structure is undoubtedly over-simplified, but a more detailed study will require additional data from either drilling or underground development.

To date the vein sheet has been traced down dip for 1,500 feet and indicated thicknesses up to 50 feet. On the North Star claim the vein shows considerable minor folding with axes striking northwest and plunges of 30° N. In the North Star adits much minor faulting is observed but the offset is not greater than a few feet. The grooves and crenulations on the fault planes indicate that at least the last movement that shattered the vein and dikes is one of dip-slip.

The pod of vein material that constitutes the Torbrit orebody has been explored for a plunge length of 1,600 feet and attains true thicknesses of up

to 200 feet although this dimension is quite variable (Figs. 2, 3, 4). The levels are designated on the basis of feet above sea level. The vein material is blind to the surface above the 1,300-foot level. On the 1,300-foot level there is 300 feet strike length of vein material with a maximum width of 50 feet exposed on the level. The vein is much broken and disturbed by two faults with right hand offsets.

The 1,150-foot level best shows the general synclinal nature of the body. The vein material is found over a 1,000 feet of arcuate length and attains

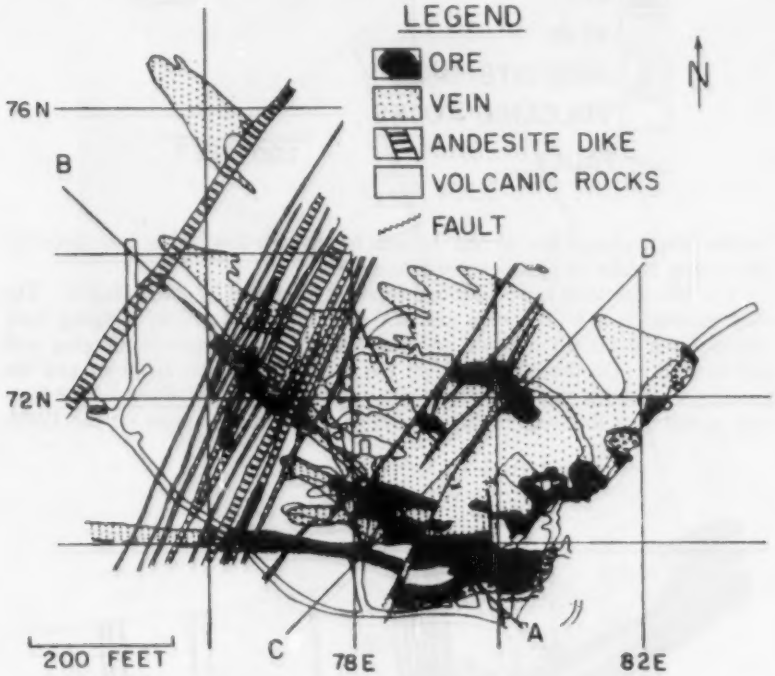


FIG. 2.

widths up to 150 feet on the level. Isolated bodies and shreds of vein are found out in the hanging wall, and this type of sporadic material is found in this same relative position down through the mine.

The 1,000 foot-level (Fig. 2) exhibits vein over an area of approximately 400 by 400 feet. It has an arcuate relatively regular footwall that is slightly disturbed by right hand faulting. The hanging wall is highly irregular with numerous fingers and tails of vein material projecting into the sheeted overhanging rock. Large horses of country rock are found within the vein material in this and lower levels of the mine. On the 1,000-foot level the

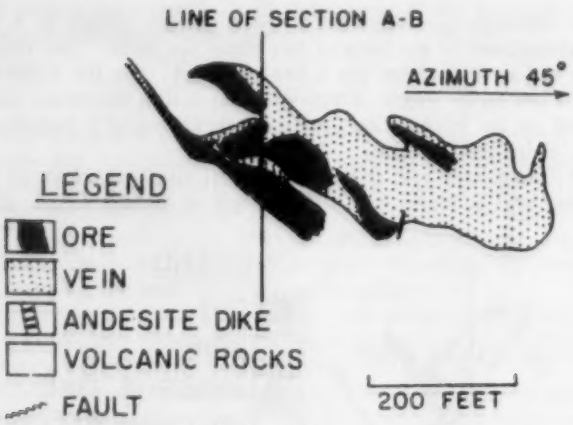


FIG. 3.

northwesterly plunge has carried the vein far enough down to be intersected by the intense swarm of post-ore andesite dikes.

The 900-foot level has a synclinal footwall disrupted by minor faults. The vein material is 400 feet wide and 600 feet from footwall to hanging wall. The andesite dikes cut the vein material about midway between hanging wall and footwall. On the 800-foot level the pod shape is less apparent and the fissure parentage of the structure is more noticeable. The plunge of the footwall is flatter in this region and an anticline that was incipient on the 1,000-

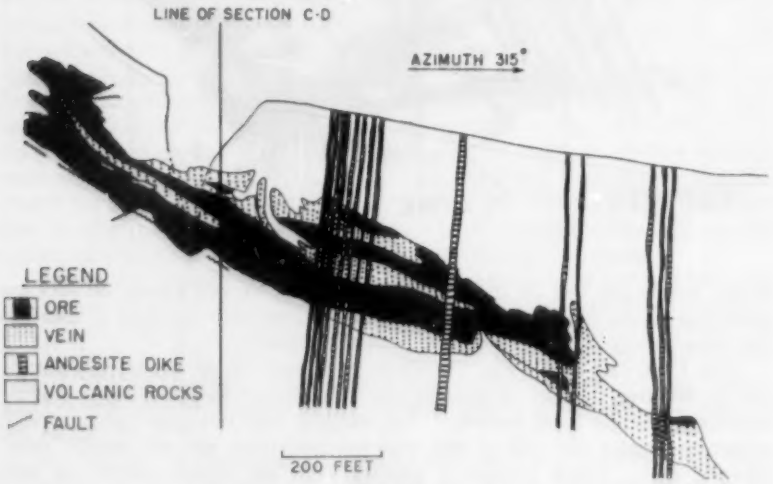


FIG. 4.

and 900-foot levels is well developed within the larger footwall syncline. The hanging wall on the 800 level exhibits much vein-filled, sheeted ground with an overall fissure character having an average strike of northwest and a steep dip west. The main swarm of dikes cut the body near the footwall on this level. The 700-foot level, although not fully explored, assumes a more fissure-

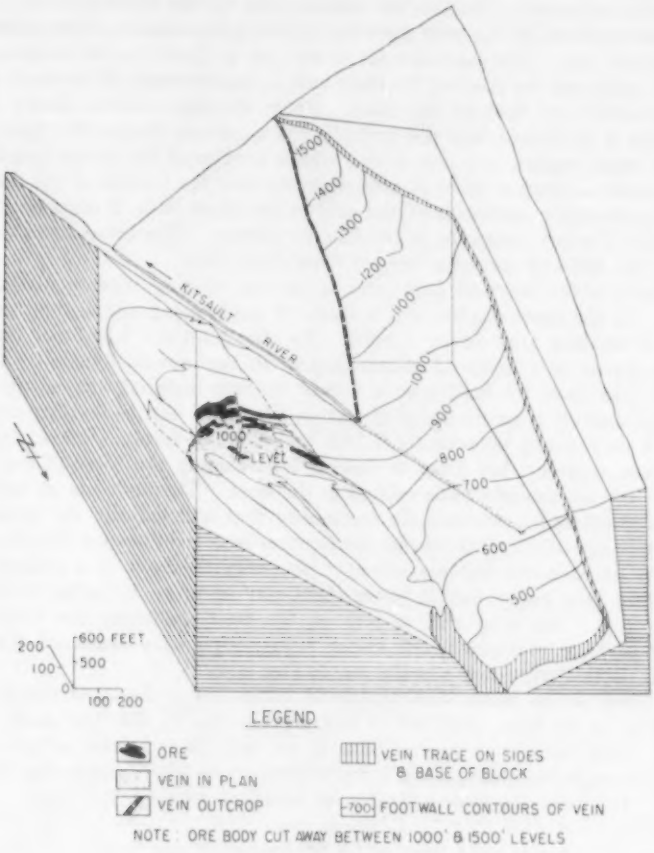


FIG. 5.

like appearance somewhat similar to the 1150-foot level. It is in general synclinal with a strike length in excess of 700 feet and vein widths over 200 feet on the level.

A cross section of the body (Fig. 3) indicates that the irregularities of outline so apparent in plan are also quite obvious in section. The fingers

and tails of vein material that project up into the hanging wall dip 45° E and therefore have the appearance of having been overturned to the west.

The relationship of the pod to the sheet of vein is shown on the block diagram (Fig. 5). The diagram is isometric and the base of the block is at 400 feet above sea level. The overall shape of the body has been somewhat generalized. The vein material between the 1,000- and 1,150-foot levels has been cut away to expose the vein in plan on the 1,000-foot level. The footwall contours of the vein sheet are shown going westward from the footwall of the pod. The outcrop trace of the vein is shown on the western slope of the valley and the trace of the sheet with a diagrammatic thickness is shown on the sides and base of the block. From the relationships shown in the diagram it is obvious that the orebody has a general fissure-like appearance in the upper region, is a pipe in the middle portion of its plunge length, and once more becomes a sheet of vein material near the bottom of the diagram. The northeastern extremity of the vein or the short limb, if compared to the Franklin Furnace structure, is blind to the surface. The behavior of the vein below the 400-foot elevation has not been determined.

Faults.—The footwall fault zone is the outstanding rupture in the mine area. As the name implies it is a series of faults along and within the footwall of the vein material at Torbrit. As shown on the 1,150-foot level the faults appear as a series of planes tangent to the arcuate footwall. On the North Star claim the fault zone is within the vein material, and on the Dolly Varden claim it is on the hanging wall of the vein. At the Torbrit mine the fault is very strong between the 1,150- and 800-foot levels. Below this level it is less apparent, but a set of fractures paralleling the footwall are noted locally and are thought to be related to the fault. The fault has an unknown displacement as no markers are recognized that will indicate the movement. The striations and undulations on the surfaces tend to indicate a dip-slip direction for at least the last movement. Generally the fault is a sheeted zone with very little gouge, but at places there may be up to 10 inches of chlorite gouge in it. No drag vein is seen in the fault indicating the absence of major post-ore movement, but minor adjustments have shattered the vein. This is particularly evident in the North Star adits.

A later set of faults with righthand offsets have displaced the footwall faults up to 50 feet. This set is best represented by the "A" fault at the mine. This break is of interest because the fault plane rotates as it is traced down through the mine giving it a different strike and variable dip on each level. The following table indicates its variations through the mine.

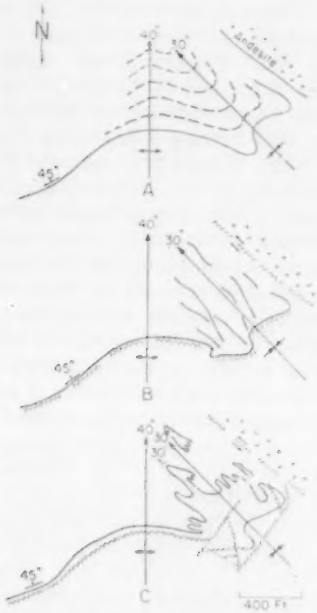
TABLE 3

VARIATIONS OF "A" FAULT

Level (ft)	Strike	Dip	Offset
1,300	N 45° W	65° W	50 feet, right hand
1,150	N 18° W	80° E	50 feet, right hand
1,000	N 30° E	80° E	50 feet, right hand
900	N 30° E	65° E	5 feet, left hand

Below the 900 foot level the "A" fault passes into the footwall and is not visible. Between the 1,300- and 1,150-foot level the "A" fault is displaced 140 feet in a right hand sense by a horizontal fault. As the strike of the vein material is the same on both levels there was no rotation on this plane that could have affected the original strike of "A" fault.

There are undoubtedly several periods of faulting in the mine area. The footwall faults are interpreted as a set that originated the sheeted and breccia zone along which subsequent mineral solutions came. The presence of un-



Proposed Evolution of the Orebody
Shown on the 1000' Level

FIG. 6.

altered gouge and fractured vein material associated with these faults indicates that some movement has continued on them even after the period of vein formation. The "A" fault is obviously post ore in age. Andesite dikes on the 900 and 800-foot levels near the shaft, are highly fractured in a zone that strikes N 10° E and is interpreted as one of minor movement sub-parallel to the joint set that gave access to the andesite dikes.

Figure 6 shows diagrammatically the sequence of structural events that gave rise to the formation of the vein sheet and pod. "A" indicates the formation of a folded fracture zone that dips generally 45° but has a minor

anticline plunging at 40° N and a tight syncline plunging 30° NW. The competent wedge of andesite is shown along the northeast side of the syncline. The next diagram, B, shows the development of fracturing along what is now the footwall, and out in the syncline. The fracturing in the syncline appears to have been of the horsetail type, due to non-uniform loading where tensional strains of the footwall zone are resolved into shear directions within the syncline. On this basis the vein sheet and footwall fracture zone is considered of tensional origin and the fracturing out from the footwall into the syncline is due to shear. The reason the strain is distributed in this manner is thought to be due to heterogeneity of the rock units. In particular the wedge-shaped pile of andesite northeast of the orebody had a marked influence on the style of folding and fracturing in the vicinity of the orebody. The fractures are sub-parallel to the axis of the syncline and in places dip 40° NE. The fracturing was most intense between the northeast margin of the syncline and the anticlinal axis, thus forming a brecciated, crudely conical zone, with its apex plunging 30° NW. Figure 6, C indicates the present appearance of the structure on the 1,000-foot level. The brecciated zone has been filled and replaced by vein material to form a pod-shaped body while the original fracture to the west has formed a vein sheet. Much solution undoubtedly modified the fracture zone and thereby opened up the structure considerably prior to deposition. This is indicated in places by the presence of crustiform banding curving around the blunt noses of vein material with no fracture going beyond the vein material. In fact this appears to be the nature of the blind upward extension of vein material on the 1.300 level.

A recurrence of stress after the emplacement of much of the vein material fractured the ground mainly adjacent to the footwall zone, but also to some extent in other parts of the structure. This ground was most receptive to ore solutions and is the main control of ore shoots in the mine. The nature of the stress field that initiated this late brecciation is highly speculative. As noted earlier, striations on the footwall zone indicate a possible dip-slip movement. This suggests that vertical movement possibly associated with the early stage of arching of Tertiary (?) time may have caused the late fracturing.

Wall Rock Alteration.—Different rock types have been affected in different ways by the mineralization. At the Dolly Varden mine the vein is within the albite andesite. On the North Star claim it is between the grey breccia and the andesite for several hundred feet and then swings entirely into the footwall andesite. At Torbit proper the vein material in general has a purple and green fragmental rock for the footwall and an andesite hanging wall. The vein material therefore does not adhere precisely to one horizon, nor is it the product of replacement of any one lithologic unit. Rather it varies between the limits of a gray breccia hanging wall to the pyroclastic rocks of the footwall, and always involves some of the albite andesite.

Along the footwall of the main body at Torbrit, partial replacement of the pyroclastic rocks gives rise to what is locally known as the "footwall breccia." Where fracturing has brought vein-forming solutions in contact with coarse breccia the fragments are replaced first and the matrix later. This

results in vein material that retains ghosts of the original breccia fragments. Peripheral to this is a zone of breccia with only the fragments replaced. As the coarse portions of the breccia are erratically distributed within the pyroclastic rocks and the fractures along the footwall do not always intersect them, the "footwall breccia" is developed only locally. It is found on the 1,150, 1,000 and 900 levels and on the western end of the footwall on the 800 level. Although this is typically a footwall feature, similar replacement of breccia material is noted in one place in the hanging wall of the extreme northwest openings on the 800 foot level.

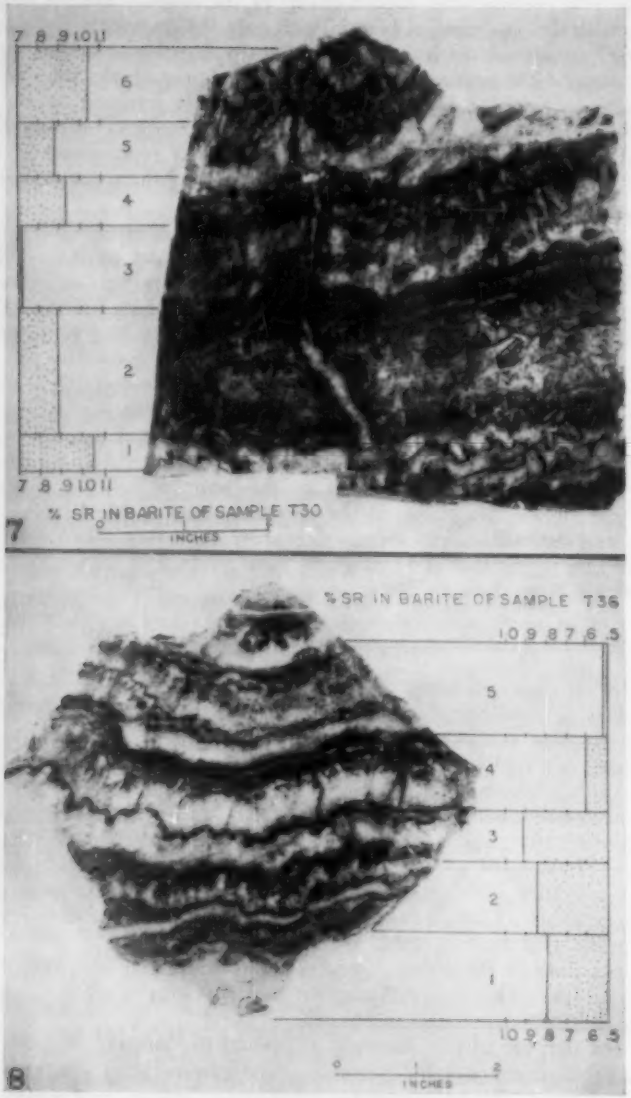
The hanging wall rocks of the Torbrit body are sheeted albite andesites that are threaded with seams of quartz, carbonate and pyrite. This rock shows bleaching, especially adjacent to the pyrite-bearing stringers. The X-ray determination of clay minerals in the alteration halo indicates that the andesite rock contains iron-rich chlorite that gives way to sericite closer to the vein. The chlorite or propylitized zone, pervades the country and is best developed in the andesite rocks. Cubic pyrite with the chlorite is generally more closely related to vein material. It appears where the matrix of the andesite shows incipient sericitization and silicification and persists up to the vein contact. The silica increases as the vein is approached and the chloritized albite crystals may persist right up to the vein or may be replaced by sericite and silica. The width of the alteration zone on the hanging wall is variable and depends mainly on the degree of fracturing. In most cases it would be safe to say that the rocks have been affected to some degree for at least 100 feet from the main body.

Mineralogy of the Deposit

Where crustiform banding is clear the criteria for the sequence of deposition is that of superposition. When fracturing has taken place, and later minerals crosscut and parallel the earlier formed bands, then the criteria of crosscutting and replacement are employed to date the depositional sequence. From a study of these ores it is evident the minerals may have been deposited at several different periods in the same orebody, and it is possible that at the same time different minerals may have been deposited in separated parts of the structure. In this study in addition to the field observations 46 polished sections were studied under the microscope, 27 large specimens were polished and studied under a binocular microscope, and 15 thin sections of vein material were studied with a petrographic microscope.

Identification of the metallic minerals was confirmed by powder photographs of each. The X-ray diffraction patterns were used to confirm the presence of all other minerals mentioned.

For the purpose of the following discussion the minerals will be divided into non-metallic and metallic minerals. The non-metallics are barite; three varieties of silica; quartz, jasper and chalcedony; calcite, and siderite. The metallic minerals are magnetite, hematite, pyrite, chalcopyrite, sphalerite, galena, tetrahedrite, pyrargarite, argentite and silver.


7 8 9 10 11
6
5
4
3
2
1
7 8 9 10 11
% SR IN BARITE OF SAMPLE T30
0
INCHES
7
% SR IN BARITE OF SAMPLE T36
10 9 8 7 6 5
5
4
3
2
1
10 9 8 7 6 5
0
1
2
INCHES
8

FIGS. 7 AND 8.

Non-Metallic Minerals

Barite.—This mineral occurs in variable amounts throughout the vein material. Later in this study a detailed description of the strontium content of the barite will be given along with a discussion of the factors that might have caused the variation.

Barite is cut by later fillings of carbonate and quartz. Where barite is involved in fracturing it apparently develops a fine granular wreath of mylonitized barite. Some such armored laths are noted surrounded by later carbonate, with no indications of replacement in evidence.

In the crustiform growths galena, hematite, and minor pyrite are deposited in the depressions and are absent on the tops of the crystals. These protected regions were more favorable for crystal growth, while the nuclei that formed on the projecting portions of the crystals may have been removed by currents.

Strontium Content of the Barite.—Crustiform deposition, as found in the Torbrit ore, affords an excellent opportunity to study variations of minerals in successive bands and thereby cast some light on the change of depositional environment with time. Photographs of the specimens from which samples were studied are shown in Figures 7 and 8. It will be noted that the number one sample in each case is taken from the earliest formed band and the last sample from the last formed. The sequence of deposition can easily be determined by the colloform growths and geometry of the barite laths.

Pure barite was separated from the samples by a simple procedure. The sample was taken from the specimen by cutting off a thin slice from which each band could be broken with pliers. The individual samples were crushed to -100 mesh, the fines washed off and the sample heated with a burner for half an hour to increase the magnetic properties of the iron oxides and sulfide. The non-magnetics were separated using a Franz isodynamic separator. These were placed in acetylene tetrabromide (s.g. $= 2.89$) and the quartz and carbonate decanted, and retained for X-ray. A few remaining galena and pyrargyrite grains were removed from the barite manually, and the sample was then ready for analysis. The crystals of barite were glass clear.

The instrument used for the analyses was a Norelco X-ray fluorescence unit equipped with a molybdenum tube which was operated at 50 kv. and 50 ma. The working curve was constructed by adding weighed amounts of reagent grade strontium sulphate to the same quality barium sulphate so as to make mixtures totalling 100 mg. These mixtures were placed in a glass holder containing a round hole as sample container, and the strontium $K\alpha 1$ peak and barium $L\alpha 2$ peaks were read for each. The curve with Sr $K\alpha 1$ plotted against percent strontium is shown in Figure 9. The peak heights are given in the units on the standard Norelco graph paper.

The barite samples from specimen T30 and T36 were analyzed and the results are shown in Table 4 and graphically in Figures 7 and 8, respectively. The results are believed to be correct to within ± 0.05 percent strontium.

As indicated by the foregoing results the strontium content of the barite varies considerably even within a short distance. This variation could be due to changes in temperature or changes in the composition of the depositing solutions.

A search of the chemical literature indicated that a study has been made of the distribution of strontium within barium sulphate precipitated from homogeneous solution at 83° C (16). The data has been recalculated and is graphically shown in Figure 10, together with an approximate curve projected into the diagram from data by Goldschmidt (15). Although 83° C is undoubtedly lower than the temperature of formation of the barite from Torbrit, the curve will serve to indicate the type of crystal-liquid relationship that would obtain during the formation of the mineral. A family of curves similar to those shown in Figure 10, could be constructed for various temperatures. With increasing temperature a solution with a given Sr/Ba ratio produces barite crystals with increasing amounts of strontium present. At any given temperature, variation of the strontium content of the solution determines the variation in the strontium present in barite precipitated from that solution. Because of the strongly ionic nature of strontium, barium and sulfate, it is thought unlikely that the chemistry of their solution and crystal relations will be complicated by the formation of complex ions.

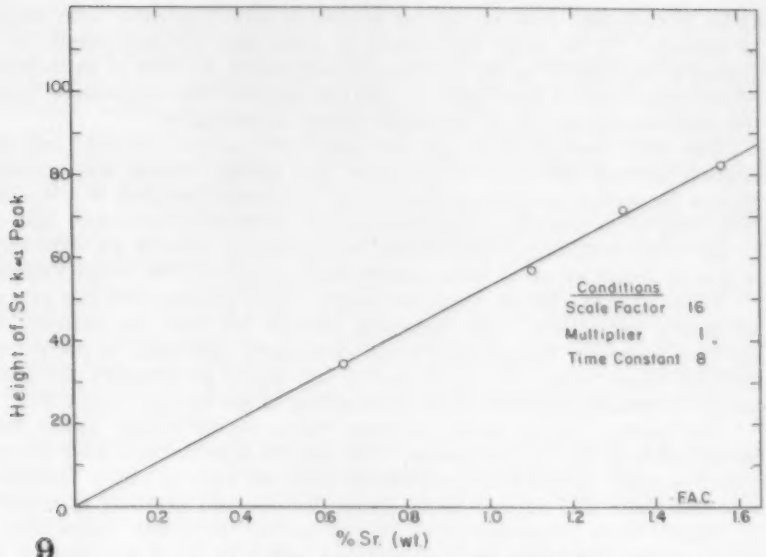
TABLE 4

STRONTIUM CONTENT OF BARITE

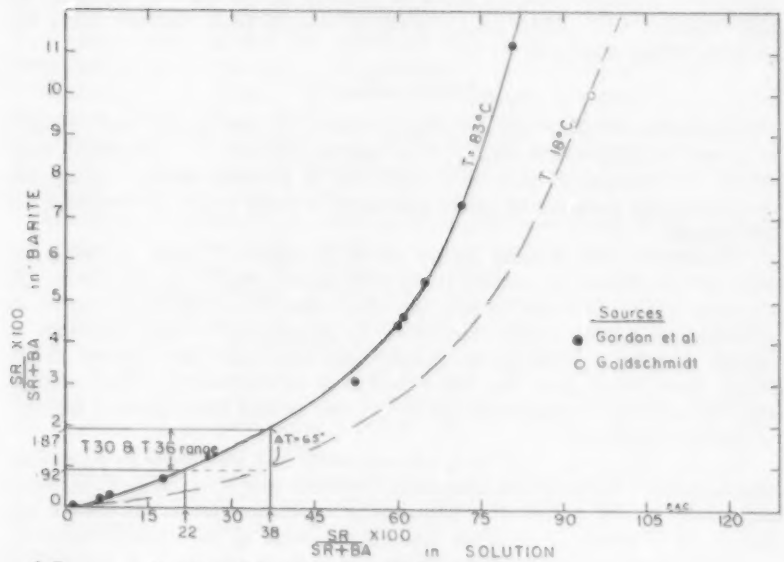
Sample	% Sr (±0.05)	$\frac{Sr}{Sr + Ba} \times 100$
T30 1B	1.05	1.87
T30 2B	0.89	1.57
T30 3B	0.72	1.29
T30 4B	0.93	1.65
T30 5B	0.87	1.57
T30 6B	1.04	1.85
T36 1B	0.79	1.40
T36 2B	0.85	1.52
T36 3B	0.91	1.63
T36 4B	0.60	1.06
T36 5B	0.52	0.92

To illustrate the variation of the solution that could produce the strontium contents found in specimens T30 and T36 if formed at 83° C, the range of composition is plotted on Figure 10 and the solution variation indicated. It is seen that if the solution ranged from 22 to 38 Sr/Sr + Ba × 100, the strontium content of the barite would vary from 0.92 to 1.87 Sr/Sr + Ba × 100. This shows that a given Sr/Ba ratio in barite requires a very much higher Sr/Ba ratio in the solution that precipitated the barite. If the solution composition were constant at say 38 Sr/Sr + Ba × 100, and the temperature varied from 18° to 83° C, it can be seen from the diagram that the Sr/Sr + Ba × 100 range found in samples T30 and T36 could be produced. In all probability in nature both temperature and composition change, and with the present data it is not possible to determine definitely which predominates, nor even what the relative importance of each might be.

In view of the possibility that the Sr/Ba ratio will increase with temperature, at a given ratio of Sr/Ba in solution, 40 samples taken from the footwall of the structure were analyzed for relative Ba and Sr content. The



9 Relation of % Sr in Barite & Sr kα1 Peak



10 Relation of Sr in Barite and Sr in Solution

FIGS. 9 AND 10.

ratios so calculated show no regular increase in strontium either with depth, or laterally. If the usual assumption is made that the temperature in a deposit at the time of formation increases with depth, the lack of an increase of strontium content with depth is negative evidence for temperature being the main determinant of the strontium content of the barite.

The silver content was known for each of the samples analyzed and the relation between this and the strontium and barium content was studied. Except for saying in a general way that barite is more prevalent in the main body than in the vein sheet, any direct relation of barite or strontium content to ore values is lacking. This would be expected in view of the difference in time of deposition of the barite and the main period of silver mineralization.

Silica.—Three kinds of silica: red jasper, coarse granular, and fine granular quartz, are present. All transitions between the three are observed in the vein material. As indicated in the paragenetic table silica is present in the first stage, along with barite, and a late quartz accompanies the main period of metallization following the fracturing of the siderite (Table 6).

Carbonates.—Calcite occurs as vein fillings in the earlier quartz and barite, and is in turn cut by siderite. The siderite is veined by a later calcite. Calcite is found as radiating growths out from the walls of earlier fractured vein material. The mineral shows strain shadows and undulose extinction.

Siderite veins calcite and is cut by late calcite. It is dark yellow-brown in transmitted light and white in reflected light. In hand specimens it is distinctly cream-yellow colored, as opposed to the pure white calcite. In addition to fracture fillings, siderite is common as the last vug filling in the vein material. In places calcite growing inward from fracture walls has a central filling of siderite.

Metallic Minerals

Magnetite.—This is not a common mineral in the deposit and typically it occurs as euhedral crystals. These crystals are noted in sphalerite, from which it is recognized with great difficulty in polished section. Magnetite is replaced and embayed by pyrite indicating an early period of deposition for the mineral.

Hematite.—This mineral occurs as small dispersed flecks in jasper, as more or less compacted masses along with jasper, and in late fractures. In the latter type it is found veining the other minerals as massive hematite or as a fibrous variety across fractures. In general, it is more abundant in regions peripheral to the main orebody, and may have been formed at different places throughout the entire period of mineralization. The relationships of hematite and magnetite are not known as they were not seen together on polished surfaces.

Pyrite.—The iron sulfide is in all cases cubic and may show an anomalous anisotropism. Some of this anisotropic material was X-rayed and confirmed as pyrite. Pyrite occurs with hematite in crustiform layers on quartz and barite. It is found in the main depositional stage of the metallic minerals, and with calcite in late fracture fillings. For these reasons it is believed to have a long time range of formation, and may have been deposited throughout

the entire period of mineralization. It is found in sericitized, silicified rocks adjacent to the deposit and often out in the chloritized wall rocks. Replacement is not extensive and successive minerals are deposited generally in fractured earlier minerals. This is the case where early pyrite is intensely fractured, enveloped and veined by chalcopyrite. Sphalerite replaces and veins the pyrite but the ability of galena to replace pyrite is far more striking. Pyrite is locally observed in the presence of the other metallic minerals in the deposit, but it is generally invaded by galena.

Pyrite is not ubiquitous in the Torbrit orebody but is more prevalent with sphalerite in vein selvedges and in the fissure sheet, where it may occur in massive seams several inches across.

Chalcopyrite.—Chalcopyrite is not common in the ores and is of localized distribution. It is more common below the 800 level than higher up in the orebody. At places in the vein sheet chalcopyrite is present in the altered footwall rocks and within the footwall portion of the vein in disseminated blebs and seams, in places constituting up to one percent of the vein material over five-foot widths.

In polished section chalcopyrite is seen as emulsoid exsolution blebs from sphalerite, and as a separate mineral phase. The emulsoid blebs of chalcopyrite are found, on staining the sphalerite, to be randomly distributed with respect to the well developed polysynthetic twin lamellae in the sphalerite. Where sphalerite and chalcopyrite are adjacent, the boundary shows mutual embayments due to a mosaic of interlocking grains of the two minerals. The polysynthetic twin lamellae, in both the sphalerite and chalcopyrite, are truncated and crosscut by grains of one another. The only conclusion satisfying these observations is that the sphalerite and chalcopyrite were deposited contemporaneously with some solid solution of chalcopyrite in sphalerite.

Chalcopyrite is replaced by galena, tetrahedrite, pyrargyrite, argentite, and native silver. The replacement of chalcopyrite by pyrargyrite, argentite, and native silver is hypogene as it is effected by embayments and veining and does not show incipient development along cleavages that is so characteristic of supergene replacement.

Sphalerite.—Sphalerite increases in abundance with depth in the orebody and toward the flanks of the structure. Some parts of the vein sheet have been found to contain up to 24 percent sphalerite over widths greater than 10 feet. The mineral varies in color from light tan to dark brown.

Sphalerite replaces pyrite and commonly contains ragged partly replaced cubes. It is intimately mixed with pyrite in stringers, especially on the fringes of the main orebody, and in the vein sheet. As indicated in the discussion of chalcopyrite, sphalerite is contemporaneous with the latter and has participated in some solid solution with it. Galena, tetrahedrite, and pyrargyrite, replaces sphalerite.

Staining with potassium chromate and hydrochloric acid solution shows extensive development of polysynthetic twins in sphalerite. Buerger (5) has indicated that such twinning on the (111) planes can be caused by applied pressure.

As shown by Kullerud (28), sphalerite when formed in equilibrium with

FeS may be employed as a geothermometer, but as no pyrrhotite is present in the Torbrit orebody this system will give a minimum temperature. Barton and Kullerud (2) have indicated that the sphalerite-pyrite assemblages can be employed as a geothermometer if the partial pressure of sulfur vapor is known. As argentite and native silver occur together in the Torbrit orebody, the sulfur vapor pressure can be calculated for a given temperature. It will be pointed out that possibly the pyrite, sphalerite, argentite, and native silver formed in equilibrium in the deposit. Whether or not equilibrium obtained, however, is impossible to say, as no criteria are known to establish proof of this condition at the time of formation of an assemblage. In this case, the assumption of equilibrium and the use of the iron content of sphalerite in the ZnS-FeS-S system, will certainly give a formation temperature closer to the correct one than any other method suggested to date. For this reason a study of sphalerite was believed worthwhile.

The method of study of sphalerites from Torbrit was a modification of that suggested by Kullerud (28). Iron sulfide, cadmium sulfide, and manganese sulfide were determined by X-ray fluorescence instead of by spectograph and lattice dimensions.

There appears to be some reason to avoid the use of lattice dimensions in the determination of iron content in sphalerite. The lattices for the Torbrit samples were determined and were similar before subtracting the CdS and MnS increments. After subtraction of the increments, and relating the remaining lattice dimension to FeS content, they indicated a wide range in FeS contents for the sphalerites. The fluorescence, as will be shown, gave less variation in the FeS content, and furthermore the amounts of FeS were lower from the determinations by fluorescence than from determinations by lattice dimensions. One would expect the fluorescence technique to indicate a higher FeS content than the diffraction method, due to pyrite, chalcopyrite, or iron oxide contamination which would increase the FeS content shown by fluorescence methods, and would not affect the FeS determined from the lattice measurements. Published curves for the cell dimensions of sphalerite plotted against FeS content appear to be straight line functions (7, 8, 25), and yet, on projection they fail to indicate the 5.406 Å dimension for sphalerite with zero FeS (38).

Smith (36) showed that natural sphalerites contain both cubic and hexagonal packing. He derived an approximate method of measuring the percent of hexagonal packing in sphalerite, and describes a technique for doing this. On application of the technique to natural sphalerites, he found a small but variable amount of hexagonal packing present in most cases. Also, he felt the indications were that the percent hexagonal packing was higher in low-temperature deposits. One specimen from Llallagua, Bolivia contained only 24.1 percent cubic packing.

The lattice variation of sphalerite with CdS, MnS, and FeS, indicated by Kullerud, are undoubtedly valid for material synthesized in the laboratory above 400° C. However, it seems one must be especially cautious in extrapolating these data into the hydrothermal region below 400° C where hexagonal packing may influence the lattice dimensions and thereby the peak positions

of the sphalerite. The present status of the problem indicates the necessity of a detailed study of natural sphalerites to determine chemical composition (especially CdS, MnS, and FeS), percent hexagonal packing, and the variation of both the cubic and hexagonal lattices with chemical composition.

The working curves for the fluorescence procedure are shown on Figures 11, 12 and 13. The curves for CdS and MnS were constructed by running synthetic sulfides of compositions indicated by the points on the curves. The curve for FeS was constructed by running analyzed natural sphalerites. Samples were not available to cover adequately the composition range, and one is needed in the six percent region to determine if the curve is a straight line. As all the other curves were straight lines, I think the best interpretation for the FeS curve, with the available data, would also be a straight line as shown in Figure 11. Pure − 200 mesh sphalerite samples from the ores were placed in a hole in a glass slide three-eighths of an inch in diameter and one-sixteenth of an inch deeper. The hole was always filled just to the top of the slide and the upper surface smoothed off. The glass plate was

TABLE 5

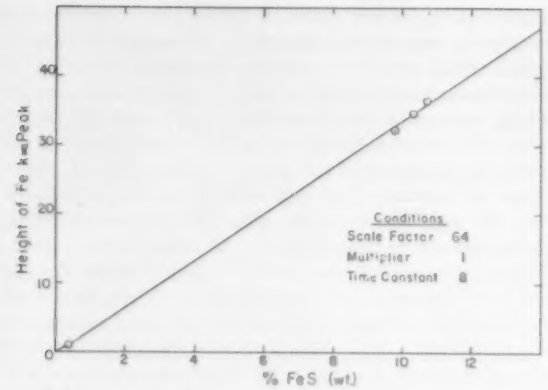
COMPOSITION OF SPHALERITES

Sample	Weight percent		
	FeS (±0.2)	CdS (±0.2)	MnS (±0.10)
N36	1.75	0.5	0.15
T40	1.75	1.0	0.10
N39	2.50	1.0	0.10
NS4	2.0	0.7	0.80
T27	2.0	0.4	0.10
Average	2.0	0.72	0.19

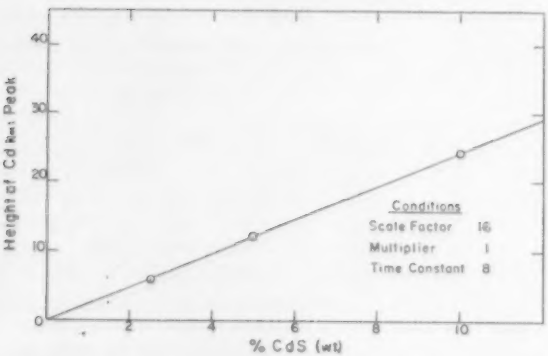
placed in the carrier and inserted into the instrument for analysis. The results for CdS are believed to be within ± 0.2 percent, for MnS within ± 0.10 percent, and for FeS within ± 0.2 percent. Table 5 gives the results of analyses of five widely separated samples. Samples N36, N39 and NS4 came from the vein sheet on the North Star. Sample T40 is from the 800 ft level and T27 is from the 900 ft level. A remarkable feature is the fairly uniform iron content of the sphalerites indicating a constant and widespread set of conditions throughout the structure during the deposition of sphalerite. I would like to suggest this indicates the co-precipitation of pyrite and sphalerite from the same solution and that the sulfur pressure was relatively constant as shown by the coexistence of argentite and silver.

A discussion of temperature of formation of the sphalerite appears later, and will not be referred to here.

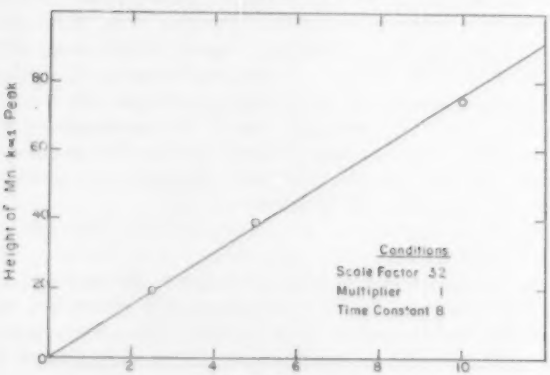
A notable feature of the Torbrit sphalerite is its high cadmium content. Warren and Thompson (42) have analyzed 122 sphalerites from western Canada and find an average of 0.55 percent CdS. They report a similar average for analyses of 10 sphalerites from the western United States. The



11 Relation of Fe K_{α_1} Peak to % FeS



12 Relation of Cd K_{α_1} Peak to % CdS



13 Relation of Mn K_{α_1} Peak to % MnS

FIGS. 11, 12 AND 13.

maximum CdS content of sphalerite is 2.1 percent and occurs in Sardinia (35), and one analysis from Torbrit of sphalerite intimately associated with pyrite gave two percent CdS. The high concentration of CdS in sphalerite has been interpreted as indicating moderate to low temperatures at the time of deposition (42, 17). Others (37, 39) disagree with the thermal control and suggest the main determinant is the availability of cadmium at the time sphalerite is being deposited. The average of 0.72 ± 0.2 percent CdS in the sphalerite of the Torbrit ores suggest a solution source somewhat different from that for the majority of deposits studied to date in British Columbia, and slightly higher in cadmium.

The average of 0.19 ± 0.10 percent MnS in the Torbrit sphalerites is lower than the 0.43 percent reported for the Coeur d'Alene district, Idaho (14). Sample NS4 shows an eight fold increase in MnS over three of the other samples. The reason for this variation is unknown.

Galena.—Galena has constituted on the average 0.5 percent of the ore mined at Torbrit. As mining proceeds below the 800 level ore has been encountered that gives mill head averages indicating 1.2 percent galena. This increase in lead with depth is associated with the previously indicated rise in zinc and copper. In the vein sheet, material containing one percent galena is encountered in thicknesses up to 55 feet below the 900-foot horizon. Thus, in general, it may be said that although galena is present throughout the structure it is more prevalent at depth in the main body and in the associated vein sheet.

Galena replaces pyrite, sphalerite and chalcopyrite. It is intimately associated with tetrahedrite and pyrargyrite. The three minerals show mutual embayment relationships and rarely the tetrahedrite and pyrargyrite are found crosscutting galena. The three undoubtedly overlapped in times of deposition.

Tetrahedrite.—The mineral is not abundant in the ore but some is always present in specimens of galena and pyrargyrite. It embays and replaces galena and is replaced by pyrargyrite and argentite. In places tiny blebs of chalcopyrite are present in the tetrahedrite and have the appearance of having been formed by ex-solution. Massive galena specimens from below the 800 level are particularly rich in tetrahedrite.

Pyrargyrite.—This silver sulfosalt is the only member of the series identified in the ores. No arsenic-bearing minerals are present and no arsenic is found in the mill concentrates at the mine. Pyrargyrite is the principal silver mineral of the ores and possibly contributes about 80 percent of the silver values. This figure is reached on the basis of the fact that pyrargyrite is not easily cyanided and only 20 percent of the values are recovered by this method. The ores mined to date have averaged on the order of 0.06 percent pyrargyrite.

The mineral is found throughout the main orebody and is concentrated in the ore shoots that are characteristically near or along the footwall, but may occur within the body or on the hanging wall. The pyrargyrite has penetrated minute fractures in the gangue and in places extends out into the altered volcanic rocks, beyond the gangue minerals. It has the characteristic

ruby-red color that is easily confused with similarly colored phases of red jasper, even by people who have worked with the ore for years. Some beautifully terminated prisms occur in tiny vugs in the gangue.

Pyrargyrite does not extensively replace earlier minerals. It is found typically with mutual embayment boundaries with tetrahedrite and galena. Rarely, however, a crosscutting veinlet is observed. This indicates that although there is undoubtedly overlap, in places some pyrargyrite was deposited later than tetrahedrite and galena. An interesting occurrence is optically oriented round blebs of pyrargyrite in galena. Why apparently isolated areas should show similar crystal orientation is unknown, however, it does suggest some ordering phenomenon possibly related to the lattices of the two minerals. Pyrargyrite was deposited along the margin of earlier minerals and gangue, obviously this physical discontinuity had been a favorable conduit.

Argentite.—Although argentite is not a common mineral in the ores, considerable is present in some specimens from above the 900 level. It is found in segmented veinlets with tetrahedrite, pyrargyrite, chalcopyrite and native silver. It replaces tetrahedrite, chalcopyrite and galena. Native silver and argentite characteristically show mutual embayments but in places there is a cuspate contact, concave toward silver, suggesting the latter continued to be deposited after some of the argentite. The general interpretation adopted, however, is that argentite and native silver are substantially contemporaneous and were in equilibrium at their time of formation.

Rarely argentite in euhedral crystals is found in vugs in the gangue. Such occurrences have been noted down to elevations of 450 feet in the orebody, thus the mineral is not restricted to the upper portions of the structure. This fact plus the geometric relationships of the argentite with such unquestionable primary minerals as chalcopyrite, tetrahedrite and galena, are taken as positive proof of the hypogene origin of the argentite. Dark gray quartz that characterizes some of the high-grade ore, is due to very finely distributed argentite in the quartz.

Native Silver.—Some of the native silver immediately below the surface is quite possibly of secondary origin, but this part of the structure in the main body is inaccessible to study. In the vein sheet no oxidation zone is present and no high lead values are encountered due to relative concentration of galena, or formation of cerussite and anglesite that might be expected if supergene agents had been active.

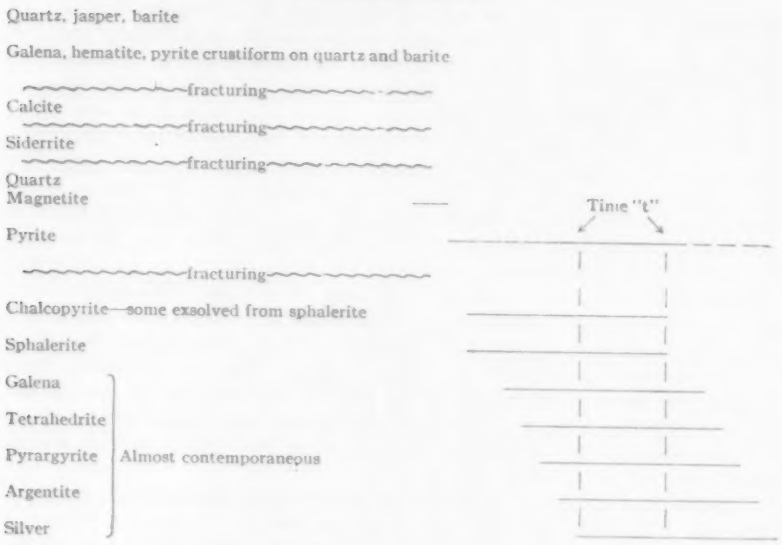
In any case, the main portion of the body contains native silver that is undoubtedly hypogene. The mineral occurs in segmented veinlets in gangue together with chalcopyrite, galena, tetrahedrite and argentite. It replaces the earlier minerals and as previously described is at least in part contemporaneous with the argentite. Native silver has been found in drilling below the 600-foot horizon which is over 1,600 feet down plunge from the apex of the body.

In summary, the order of deposition of the minerals is shown graphically in Table 6. It will be noted that galena, hematite and pyrite appear early as crustiform deposits on quartz and barite. Whether or not this period of

metallic mineral formation overlaps with the later main period is not known, so no time line can be drawn to show the relationship of the two periods. As mentioned earlier, hematite occurs also as a late stage mineral, and may have been formed at all stages in the depositional sequence. As the main period of metallic mineral formation is of particular interest, a diagrammatic representation of the time span for the formation of each mineral is shown by the length and position of the line opposite it. The line starting furthest to the left is earliest, that projecting furthest to the right is deposited last. The chart has been constructed from the polished section data to show that for a time span "t" it is quite possible to have pyrite, sphalerite, argentite, and

TABLE 6

PARAGENETIC SEQUENCE



native silver precipitated together. How much absolute time would be represented by the hypothetical "t", and what portion of the sphalerite found in the deposit was formed during this interval is not known. The fairly uniform FeS content of the five sphalerites analyzed suggests that they were formed within or near this interval.

GENESIS OF THE DEPOSIT

According to the Lindgren classification (30), the Torbrit ore deposit exhibits characteristics of both epithermal and mesothermal deposition. The host rocks are volcanics that have been propylitized and sericitized. They occur in the circum Pacific belt where so many epithermal deposits are found.

The ore textures show evidence of abundant open-space filling and crustification. The vein material is brecciated, split, and chambered as is characteristic of epithermal deposits. The mineralogy is similar to hot springs in some respects in that chalcedony, quartz, calcite, barite and pyrite are present. The colloform banding indicates colloidal deposition of much of the silica. Of the ore minerals native silver, argentite, pyrargyrite, and tetrahedrite are typical of certain epithermal deposits.

The presence of siderite, and lead-zinc and copper minerals in fairly large amounts suggest mesothermal affinities. The replacement of wall rocks and gradual transition form vein material through a sericitized and silicified zone into wall rock suggests a higher intensity level than found in the frozen-walled veins formed under epithermal conditions.

Depth of Formation.—It is possible from structural and stratigraphic considerations to arrive at an approximate depth of the deposit at the time it was formed. The assumption made is that the pile of sediments and volcanics that overlay the deposit is equal to the total thickness of rocks now above the body. This includes the rocks from the mine to the Kitsault Glacier, a total thickness of 8,000 feet. There may have been more than 8,000 feet of rocks originally present but some of them would be erroded during uplift so the figure used is reasonable in view of the available data. As the sequence is plunging 30° N, the effective cover over the deposit would have been on the order of 10,000 feet. This is equal to 300 atmospheres of hydrostatic pressure by making the reasonable assumption that the solution had a density of one during the period of ore formation. I do not think that any interpretation could result in a pressure of less than 200 atmospheres. The figure is in good agreement with the proposal of between 140 and 400 atmospheres pressure suggested by Lindgren (30) for mesothermal deposits.

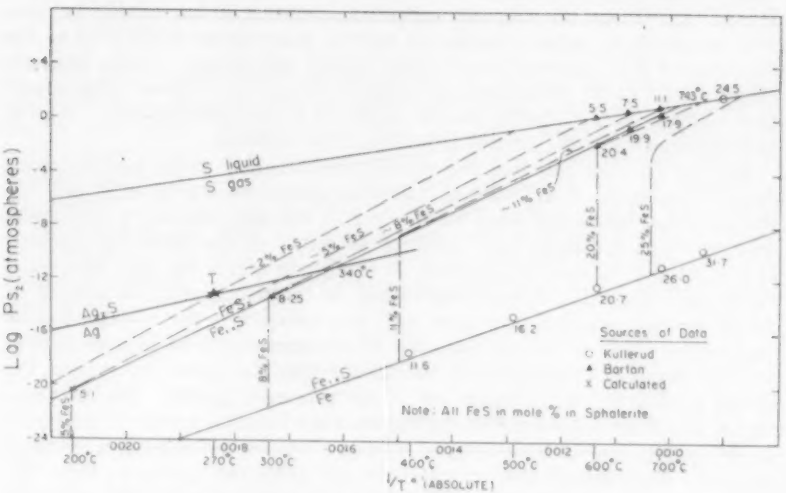
Temperature of Formation.—Students of ore deposits for many years have sought ways to determine the temperature of formation of mineral deposits. Ingerson (26) has reviewed the various techniques, and compiled considerable data on the subject. In the case of the Torbrit deposit several approaches will be considered.

The melting point of a mineral in a deposit gives the maximum temperature that is possible after the particular mineral is formed, but does not necessarily indicate a limit for earlier minerals. On the other hand, as the minerals are formed from hydrous fluids, undoubtedly far below their melting points, then the point of fusion of any mineral in an assemblage may be a safe upper limit for temperature of formation. In the ores under consideration, the presence of pyrargyrite indicates an upper limit of 483° C plus a small correction for pressure (12). As the deposit was at a depth of about 10,000 feet, employing a geothermal gradient of 9.0° C/1,000 feet (33) the probable minimum temperature was 90° C. On the other hand, as this was an area of much igneous activity, data given by Van Orstrand (41) for temperatures in Pleistocene volcanics in Oregon may be closer to the truth. Although this gradient in Oregon is irregular it approximates 15° C/1,000 feet down to 3,500 feet, from a surface temperature of 20° C. If a similar gradient applied when the Torbrit body was formed, a minimum temperature

of 150° C is indicated. By these means the range of formation temperatures can be inferred to lie between 150° and 483° C.

As mentioned earlier, the iron content of sphalerite can be used as a geothermometer under certain conditions (28). The ZnS-FeS system will indicate the correct temperatures only if the sphalerite is formed in equilibrium with pyrrhotite. In the Torbrit ores no pyrrhotite is present, but the iron content in sphalerite will at least give a minimum temperature and could conceivably give the correct value. The average of five Torbrit sphalerites (Table 5) is 2.3 mole percent (2 wt. percent) FeS, and this indicates a temperature of formation greater than or equal to 80° C.

Sphalerite is present with pyrite in the deposit, and published data on this assemblage are lacking. However, Barton (personal communication)



PART OF THE SYSTEM ZnS - FeS - S

FIG. 14.

has kindly supplied author with data on the partially studied FeS-ZnS-S system upon which he and Kullerud are presently working. These data plus values from Kullerud (28) enabled the construction of Figure 14. The equilibrium fields of FeS-Fe; FeS_2-$Fe_{1-x}S$; S liquid-S gas; and Ag_2S-Ag are calculated from data supplied by Darken and Gurry (10). The FeS content of the experimentally determined and the calculated points are shown on the diagram. As the entire diagram is in the stability field of sphalerite the percentages of FeS in equilibrium with FeS and FeS_2, are contoured as shown. The position of the contours are dashed in to indicate incomplete knowledge of their position. The contours in the pyrrhotite field are established from experimental work, whereas those in the pyrite field are placed

by experiment, and on the basis of calculations by H. D. Holland (personal communication). It will be noted that below 600° C the iron content is independent of sulfur pressure until the pyrite field is entered and then there is a marked decrease in the solubility of FeS in sphalerite with increasing sulfur pressure.

From the interpretation of paragenetic relationships it appears that at least in places in the deposit argentite, native silver, pyrite, and sphalerite may have been in equilibrium. As sphalerite averages 2.3 mole percent FeS, the intersection of the 2 percent contour and the argentite-silver join at the point "T", gives a temperature of formation of 270° C and a sulfur pressure of 10^{-13} atmosphere. In view of the fact that the position of this contour in the pyrite field is not experimentally defined, it could vary from this position. The greatest possible variation would indicate a temperature range from 230° to 310° C. From the diagram under consideration it can readily be seen that variations in sulfur pressure as well as temperature could account for the range of FeS contents found in the Torbrit sphalerites. It also indicates clearly that if pyrite rather than pyrrhotite is present in a deposit great errors may result if the FeS-ZnS system is employed as a geothermometer. Barton and Kullerud (2) have already pointed out this difficulty.

Buerger (6) has indicated that some sphalerite-chalcopyrite solid solutions unmix between 350° and 400° C. This temperature range is valid only for the particular specimens used by Buerger as the temperature of dissolution will vary with sphalerite from different deposits. If the unmixing temperature is defined as that temperature on cooling at which the first exsolution takes place, then this theoretically should be the temperature on heating at which the last exsolved bleb goes back into solution, if the system remains unchanged. Two of the determinants of the temperature of homogenization are, the depth of penetration of the solidus into the solvus curve, and the extent of chalcopyrite diffusion out of the sphalerite grains. The temperature at which the solidus and solvus intersect is a function mainly of the fluxes in the system, and in hydrothermal solutions this is undoubtedly a complex variable. Diffusion of chalcopyrite from the sphalerite grains to form discrete segregates, has the affect of shifting the composition of the sphalerite grains in the direction of decreased chalcopyrite content. The chalcopyrite exsolved in such a grain will re-dissolve at a lower temperature than the original, and will thus give a minimum temperature. It is impossible to tell whether interlocking grains of chalcopyrite and sphalerite have been formed from exsolution, or by contemporaneous precipitation. For this reason one is never certain, when determining the temperature, if only the sphalerite grains, or the entire aggregate of sphalerite and chalcopyrite, should be homogenized. An interesting study of the Aberfoyle deposit in Tasmania (31) shows that on the basis of iron content, the sphalerite formed from 585° to 615° C, and the initial temperature of dissolution of chalcopyrite in sphalerite was at 625° to 650° C. This is an excellent example of both approaches yielding comparable results. As dissolution experiments have not been conducted on the exsolved chalcopyrite blebs in Torbrit sphalerite, their temperature of formation is unknown. From the iron content of the sphalerites, however, it can be inferred that dissolution will take place at about 270° C.

The following is a tabulation of temperature of formation data on the Torbrit deposit. The temperatures of epithermal and mesothermal formation are included for the purposes of comparison.

TABLE 7

TEMPERATURE OF FORMATION DATA

Source	Minimum (° C)	Maximum (° C)
Normal geothermal gradient to 10,000 ft	90	—
Geothermal gradient in volcanic region to 10,000 ft	150	—
M. P. of pyrargyrite (at 1 atmos.)	—	483
Sphalerite (FeS-ZnS)	80	—
Sphalerite (ZnS-FeS-S / Ag$_2$S-Ag)	230	310
	(270° C indicated)	
Epithermal	50	200
Mesothermal	175	300

Time of Formation and Magmatic Source.—From the structural relationships displayed in the area a relative time for the formation of the deposit can be ascertained. An absolute time is less easily determined and involves certain assumptions. The orebody is later than the Hazelton rocks, and the feldspar porphyry intrusion, and earlier than the andesite dikes. With this information, and equating the feldspar porphyry in time with the last phases of the Coast Range, and the andesite dikes with Tertiary vulcanism, fairly good limits can be placed on the time of formation. This information is shown in Table 8, where the ore deposition is shown as late Cretaceous to early Tertiary.

TABLE 8

TIME OF ORE DEPOSITION

Time	Event	
Tertiary (?)	Andesite dikes intruded	
	Ore deposition	Silver-lead
		Copper-gold
Cretaceous (?)	Feldspar porphyry intruded	
Jurassic (?)	Hazelton group deposited	

In view of the importance of the time of emplacement of the igneous rocks in this discussion, further consideration of the matter seems worthwhile. On the basis of the geology of the Upper Kitsault, the feldspar porphyry is later than the folding of the Jurassic (?) Hazelton group. It is in turn cut by the andesite dikes, which are dated as Tertiary (?) on the basis of composition, structural relations, and an observed transition of a similar dike into the Tertiary volcanics at Alice Arm (18). In order to determine the relation of the feldspar porphyry to the Coast Range intrusive, information must be sought outside the area. The map of the Portland Canal area (18), shows

a belt of quartz porphyry and quartz diorite dikes that is sub-parallel to the contact of the Coast Range batholith from Mt. White Fraser to Mt. Dickie and then disappears under the cover of the Cambria Snowfield. Hanson suggests that the dikes in this zone may be the top of an elongated stock intruded into a zone of fracture parallel to the contact of the batholith, and co-magmatic with it. He dates these rocks as post-Coast Range intrusives. I would like to point out that if the trend of the intrusives is continued across the snowfield, it emerges precisely where the feldspar porphyry appears from under the Kitsault Glacier. It seems certain that the intrusives are controlled by the same structural break, and it may be one of some metallogenic significance. It is on this basis that the feldspar porphyry is dated with the last phases of the Coast Range intrusives in late Cretaceous time.

The presence of chalcopyrite and gold in the structures within the feldspar porphyry, and the absence of gold with the chalcopyrite in the silver-lead veins of the volcanic rocks suggests a zonation about the feldspar porphyry. The timing of the structures with the stages of deposition is remarkable. The structures in the feldspar porphyry appear to have been formed first, at the time when solutions to form the higher intensity deposits could gain access to them. The differently oriented structures in the Lower Volcanic formation were mineralized by later solutions bearing silver, lead, zinc, copper, and lacking gold. This relationship strongly suggests that the feldspar porphyry, and the two periods of mineralization are genetically related to the same magma source as the Coast Range batholith. However, in view of the continued volcanism from Jurassic time to Pleistocene in the Western Cordillera, a volcanic source for the solutions must be considered possible. Certainly the Lower Volcanic formation of the Hazelton group is the most favorable host rock, as are volcanic rocks for many deposits of this type in the western United States.

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Feb. 9, 1959

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A METHOD FOR DETERMINING SOLUBILITY AT HIGH TEMPERATURES AND PRESSURES

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ABSTRACT

The importance of the part played by solubility in the transportation and deposition of ore sulfides can only be assessed by experiment because thermodynamic extrapolation of solubility to high temperatures and pressures is unreliable. In the method of solubility determination described, zinc sulfide, tagged with Zn^{65}, was dissolved by water in a bomb, the sulfide having been sealed into a small porous capsule to prevent solid particles from circulating in the bomb chamber. The gamma-radiation intensity of the dissolved ZnS was measured with a scintillation detector placed near the bomb. The solubility was obtained by reference to a standardization curve. The contents of the bomb were at a pressure of about 4,500 psi during the experiment and the effective temperature of solubility was $130 \pm 5°$ C.

The accuracy of the method has not been fully established, but the writer suggests improvements in procedure and apparatus that he believes will make possible the determination of useful data for a wide variety of solid-aqueous systems at almost any pressure and temperature assumed for the formation of hydrothermal deposits.

INTRODUCTION

THE very low solubility of many ore-forming sulfides is considered by many geologists to be a major weakness of those theories of ore genesis which state that ore sulfides are transported in an aqueous solution. According to calculations (8), the solubility of sulfides in water increases as the temperature increases, but even at temperatures assumed for the formation of hydrothermal ore deposits, the calculated solubilities, if accepted, are so low that it is highly improbable that endogenic processes can provide water in sufficient quantities to form ore deposits of base metal sulfides. On thermodynamic grounds, Gibson (3) has predicted increases in the solubility of sulfides with increased pressure, but the probable magnitude of the increase for any particular sulfide is uncertain.

Accurate thermodynamic data form a reliable basis for extrapolating solubilities to higher temperatures, provided one important assumption is valid. The assumption is that the chemical species in any particular system, for instance metal sulfide-water, are the same at the temperature for which solubility is calculated as they are at the temperature for which thermochemical data and equilibrium constants are available. Inasmuch as it is not known what chemical species may form at higher temperatures, calculated solubilities may be quite different from the true solubilities, in which case no sweeping geological inferences can be drawn from them. Similarly, the

calculated effects of pressure are less reliable as the pressure increases. Considering, also, the probable complexity of ore-bearing solutions, solubility calculations must at present be considered of very limited value to geologists. If solubility is to be given a just consideration as a possible mechanism of ore transportation, it is clear that more data for high temperatures and pressures must be obtained.

The results of an investigation into a radioactive tracer method for determining solubility are described below. Parts of the apparatus were found not to be entirely satisfactory and accurate data were not obtained in the experiment to be described. Nevertheless, the results of the investigation are interpreted as indicating that the method, if refined, can provide information of value in solving certain problems of ore transportation.

OUTLINE OF THE RADIOACTIVE TRACER METHOD

The feasibility of the "tracer" method of solubility determination depends upon the high penetrating power of the gamma radiation. Thus the concentration of a gamma-emitting sulfide in a solution within a thick-walled high temperature-pressure vessel can be determined by measuring the radiation intensity with a detector placed outside the vessel and comparing this intensity with the intensities from a set of solutions of known concentration.

APPARATUS

Part of the apparatus is shown in Figure 1. The bomb, machined from Haynes' Alloy No. 25 following the description by Tuttle (*7*), can withstand simultaneously a pressure of 60,000 psi and a temperature of 700° C. provided the seal is kept below about 200° C. The porous solute capsule was made from a crystal-drying slab by drilling and grinding. The radioactive solute in the capsule was separated from the porcelain cement ("Sauereisen No. 1") [1] by a wad of fiberglas wool. A spiral heating element and a split cylinder refractory support constitute the essentials of the furnace: the bomb was heated from one side only so that the other side could be placed close to the lead shielding. The lead shielding was composed of slabs 4" × 4" × ½". The bomb and furnace were wrapped in asbestos cloth (not shown) to reduce temperature differences within the bomb. In order to protect the crystal detector from heat radiation, the detector probe was wrapped in aluminum foil which was also placed over the bricks on the side facing the bomb. Crinkled paper was used as a heat insulator. The detector probe contains a 2½" sodium iodide crystal and its photomultiplier and was connected by a shielded lead to the rest of the equipment.[2] The output was fed into a Leeds and Northrup Speedomax recorder. The counter time constant switch had insufficient damping effect upon the movement of the recorder pen, consequently it was necessary to place a damping capacitance of 120 microfarads across the recorder input in order to reduce the fluctuations to a reasonable

[1] Purchased from Fisher Scientific Co. Ltd.

[2] The detector probe and associated equipment was manufactured by Eltronics Inc., Philadelphia, Pa., as a portable unit for use in a vehicle.

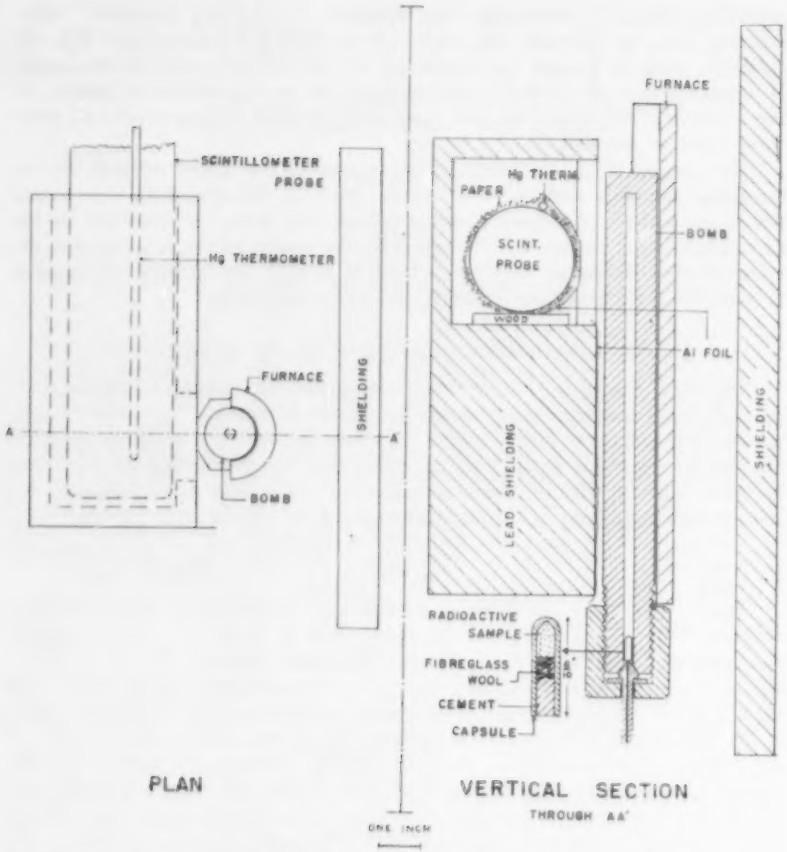

FIG. 1. Some parts of the apparatus. The bomb is in position for an unshielded reading.

level. The mercury thermometer was used to indicate approximately the temperature of the probe. The following high pressure equipment [3] was also used: high pressure tubing, a straight coupling, a Bourdon gauge (range zero to 40,000 psi) and a valve. Temperature measurement and control was achieved by means of a "Temcometer." [4] This is a simple bimetallic strip power input controller incorporating, in addition, a thermocouple-galvanometer circuit which registers temperature to the nearest 10° C. The temperature of the bomb was calculated from potentiometer-thermocouple measurements. As several hours of experiment are required to obtain a desired temperature,

[3] Manufactured by American Instrument Co.
[4] Purchased from Canadian Laboratory Supplies Ltd.

when using a Temcometer-controlled furnace, a direct control instrument would be much more satisfactory for experiments during which changes of temperature are to be made.

PRINCIPLES

It is assumed that when the solvent, and the capsule containing the radioactive solute, have been placed in the bomb, the solute begins to dissolve and diffuses through the walls of the capsule. It then spreads uniformly throughout the solvent by diffusion and convection and eventually saturates the solution. During this process the solution gradually becomes richer in radioactive solute, the presence of which is detected by the scintillation crystal. As saturation is approached, the difference between successive readings becomes smaller until, finally, there is no further change in radiation intensity and saturation is assumed to have been reached. The solubility of the solute can then be determined by comparing the final intensity with the intensities from a set of standard solutions measured under similar conditions.

The purpose of the solute container, or capsule, is to provide a permeable enclosure for the solute, allowing solute and solvent to meet but preventing any solute particles from going into suspension. Should this happen and particles of radioactive solute be carried upwards by convection, an erroneously high solubility would be measured.

In choosing a radioactive tracer the following requirements should, if possible, be satisfied. a) The isotope should be gamma-emitting, preferably of high energy. Other forms of radiation have low penetrating power and are therefore unsuitable where half-inch metal walls must be penetrated. b) The half-life of the isotope should be reasonably long—a month or more. If the half-life is too short, complications will arise in the comparison of readings taken over a period of days. c) The proportion of radioactive isotope present in the sample should be great enough to provide measurable gamma-ray intensity at the expected sulfide concentration. d) The isotope should be free from contamination by other elements. Because only a very short-lived gamma-emitting isotope of sulfur exists, the general applicability of this method to the study of sulfide solubility depends upon the availability of suitable isotopes of the metals.

The accuracy of the tracer method depends largely on the validity of the following assumptions: a) No chemical or physical factors interfere with the system under study. b) Standardization and experimental conditions are essentially the same. c) The solute is in true solution.

PROCEDURE

For the experiment, zinc sulfide of reagent grade was irradiated in the NRX reactor at Chalk River, Ontario, receiving a total of 4.16×10^{19} neutrons/cm^2. ZnS was chosen because one of the natural zinc isotopes, Zn^{64}, can be altered by thermal neutron capture to give a reasonable quantity of the gamma-emitting isotope Zn^{65}, which has a half-life of 250 days. The long half-life and the relatively high energy gamma radiation of Zn^{65}, and the

relatively greater solubility of ZnS—compared with other base metal sulfides —make radioactive ZnS very suitable for experiments such as the one described here. The irradiated sample was not tested for purity. In order to keep the chemistry as simple as possible, water was chosen as the solvent.

About .02 gm of ZnS, having a radioactivity of about one millicurie, was placed in the capsule and covered by a wad of fiberglas wool to prevent the sulfide from mixing with the cement. The resistance of the cement to water was greatly increased by treating it with acetic acid, as suggested by the manufacturers. The bomb was filled with water, and the capsule containing the radioactive ZnS was placed in it. A short length of tubing, also filled with water, was then connected first to the bomb and then to the rest of the high pressure system; thus, because of the narrow ($\frac{1}{16}''$) internal diameter of the tubing, no fluid was lost from the bomb. The furnace was then turned on. As the temperature of the bomb increased, the pressure also increased due to the expansion of the water. By slightly opening the valve at intervals during the temperature rise, the pressure was kept down to about 4,500 psi as indicated on the Bourdon gauge. In experiments of this type, the pressure of the system must be kept above the vapor pressure of the water, otherwise a vapor phase may form at the top of the bomb and cause erroneously low radiation readings.

The sensitivity of the method is greatly affected by the spatial relations between the crystal detector, the sources of radiation and the shielding. The most sensitive arrangement will give a reading that is as large as possible compared with the background radiation. The strongest source of background radiation is the solute in the capsule, thus a compromise must be made between the ideal position for measuring the radioactivity of the solution (near the center of the bomb) and the maximum shielding from the capsule. The final arrangement, shown in Figure 1, was arrived at largely by experiment with two bombs, one containing only radioactive solution and the other containing only the capsule and its radioactive contents. The great thickness of lead beneath the crystal was found to be necessary in order to shield it adequately from the radiation of the capsule. Because of possible damage to the detector probe by heat conducted through the lead bricks the bomb could not be left against the bricks as shown in Figure 1. This position was established only to take readings; at other times the bomb was placed about an inch-and-a-half away, and a sheet of aluminum foil, reinforced with cardboard, placed between the bomb and the probe.

Radioactivity of the solution was measured by taking two consecutive readings. The position of the crystal was kept fixed throughout the experiment. One reading was obtained when the lead shielding between the crystal and the top of the bomb was removed and the bomb placed against the bricks (Fig. 1). A second "shielded" reading, necessary as a comparison to eliminate the effects of instrument drift and changes in background radiation, was made with two half-inch lead bricks between the crystal detector and the bomb. Space for the additional brick was provided by tilting the bomb outward slightly; previous experiment showed that this arrangement caused no detectable change in the intensity of background radiation from

the capsule. The difference between the two readings gave a measure of the radioactivity of the solution and hence the concentration of the ZnS. Four or more "differences" were obtained in about an hour and, when averaged, were represented as a point on a graph of concentration versus time. Four such points were obtained and these are shown in Figure 2. Owing to difficulties with the electronic circuit, no further points could be obtained; however, it was possible to estimate the "plateau" radioactivity by graphical extrapolation and hence the solubility by referring the radioactivity to the standardization graph.

The standardization curve was based on measurements using solutions of known concentration at room temperature and pressure, and the same ZnS-charged capsule as was later used in the experiment. The weakest standard solution (.001 gm/liter) could not be detected above background radiation.

RESULTS

The pressure varied between 4,000 and 5,000 psi during the experiment. According to the Temcometer galvanometer, the temperature at the outside wall of the bomb, seven-and-a-half inches below the top (the position of the Temcometer thermocouple), fluctuated between 250 ± 10° C and 260 ± 10° C. The temperature of the solution in the bomb during the experiment was inferred by placing a thermocouple probe in an empty bomb and by calculating the temperature from potentiometer measurements. The temperature of

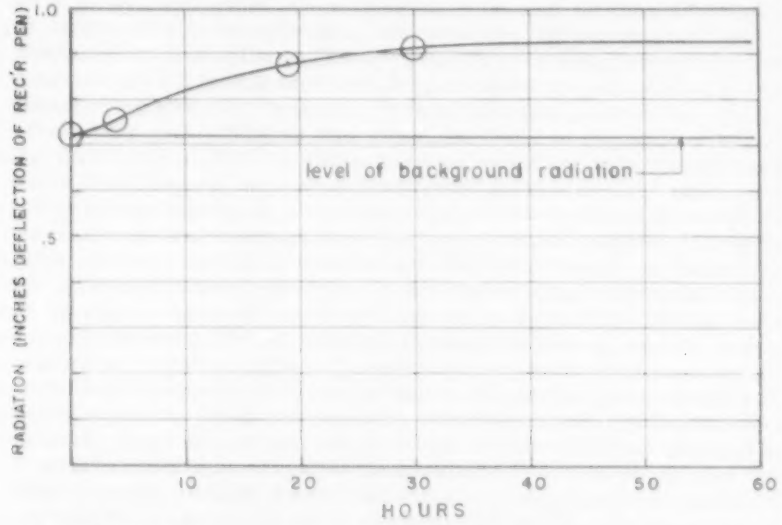

FIG. 2. Graph showing change of ZnS concentration (in terms of radiation) during the experiment. Heat was turned on at zero time but temperature equilibrium in the bomb was not reached until about four hours later.

the solution opposite the Temcometer thermocouple was 270° C (260° C at the same time at the Temcometer thermocouple). At the top of the bomb, the solution was about 310° C and at the capsule, 130° C. The temperature at the capsule is considered to have varied from this by not more than 5° C during the experiment.

Figure 2 shows the change of radioactivity of the solution with time. Equilibrium is estimated to have been reached at 50 to 60 hours, giving a value close to .95 inch deflection of the recorder pen (.725 inch of which was due to background radiation, mostly from the capsule). According to the standardization curve, .95 inch corresponds to a solubility of .004 gm/liter. Taking into account possible errors in the measurement of radiation, this figure is subject to a maximum error of 25%. According to Verhoogen's calculations, .004 gm/liter corresponds to solubility at about 117° C.

After the experiment the capsule was found to be unchanged, and although the cement had softened, it was still all in place and is not thought to have allowed any sulfide particles to escape.

INTERPRETATION AND DISCUSSION

It is important that the standardization curve should be based on measurements of standard solutions under conditions as nearly as possible identical with experimental conditions. In order to agree with the conditions of standardization, "active" and ordinary atoms that dissolve during the experiment must be in solution in proportion to their concentration in the undissolved solute. This will be true if all, or most, of the solute dissolves or if the solute was prepared by combining the radioactive metal with sulfur. In this experiment, radioactive ZnS was prepared by irradiation of the compound, so it is possible that permanent energy changes took place at the site of neutron capture. If the energy state of "active" zinc atoms in the lattice is increased, or if they form part of a new compound, such as $ZnSO_4$, they may dissolve preferentially and cause a high apparent solubility. But since only ions that are exposed to the solvent can dissolve and since, when saturated, the number of "active" atoms in solution is high compared to the number on the surface of all ZnS particles, "active" atoms and ordinary atoms will be in solution very nearly in proportion to their concentration in the sample. In experiments using more highly activated and less soluble material than ZnS, the error may be significant if only a small fraction of the solute dissolves. In general, it must be considered more satisfactory to use tagged samples prepared so as to avoid chemical contamination or damage to the lattice structure. It should be mentioned that the number of zinc atoms involved in the nuclear reaction leading to radioactive Zn^{65} is relatively very small, so that the overall effect on the solubility of ZnS will, at worst, also be very small. The fact that some of the solid ZnS was dissolved during the experiment whereas in standardization the amount was the same for each standard solution, represents a discrepancy, but in this case a very minor one, because only one five-hundredth of the initial solid in the capsule is thought to have dissolved. The discrepancy resulting from the fact that the standardization measurements were made at room temperature and pressure is thought to be minor.

According to Schiff (5), the concentration of a salt in a liquid cannot anywhere be greater than the solubility of the salt in the vicinity of the solute supply, hence the effective temperature of saturation in this case cannot be higher than $130 \pm 5°$ C. According to Lewis and Randall (4), the Soret effect may operate in solutions under a temperature gradient. In cases where this effect has been investigated (6), a higher concentration is found at the lower temperature. The writer does not know whether a similar effect would occur in a solution that is in contact with undissolved solute—as is the case in this experiment; nevertheless, the possibility should be considered.

A difference of at least two degrees centigrade existed between opposite surfaces of the bomb chamber. In a system that was otherwise gravitationally stable, the two degrees difference may have caused a slow circulation of the solution, thus speeding the attainment of the equilibrium.

The accuracy of the results depends largely on the degree to which the assumptions, previously mentioned under "Principles," are valid. The validity of the assumption that no chemical or physical factors interfere with the system under study is dealt with under two headings: Radiochemical factors, and Interference from the apparatus.

Radiochemical Factors.—a) Zn^{65} decays to Cu^{65}. The experiment was made about a year after irradiation; therefore approximately 10^{-17} gm of Cu^{65} had accumulated in the solute sample. Compared to 3×10^{-8} gm of ZnS present in the saturated solution, the chemical effect of this minute amount of copper can be considered negligible. b) According to Friedlander and Kennedy (2), it is unlikely that isotopes other than those of zinc and sulfur are produced during irradiation of the ZnS sample by thermal neutrons; contamination from this source is therefore unlikely. c) The possible effects of damaged crystal lattice have already been discussed.

Interference from the Apparatus.—Interference may occur in two ways. 1) If zinc ions are adsorbed on the walls of the bomb, a high apparent solubility will be measured. In a trial run with a bomb that had been used in other high temperature experiments, adsorption on the oxidized wall was appreciable and undoubtedly could have affected the accuracy of the results. In the final experiment a new bomb was used and afterwards the chamber walls were found to be as smooth and shiny as before and no radioactivity could be detected. 2) As already noted, the bomb appeared to be uncorroded after the experiment; however, it is possible that at higher temperatures and pressures, and using different solutions, chemical interference would have to be considered. The connecting tube, which was not made of stainless steel, was definitely oxidized and had adsorbed, or accumulated by precipitation, detectable quantities of zinc. Considering that this concentration of zinc was immediately below the capsule and not at the "measured" end of the bomb, it is not thought to have affected the final results.

The assumption has been made that the radioactivity from the top of the bomb chamber represents the radioactivity of ZnS in true solution, or very nearly so. If solid particles of ZnS had become suspended this assumption would not be valid. Frederickson and Cox (1) have shown from their experiments that particles of quartz may be dislodged from the solute sample,

at elevated temperatures and pressures, and be withdrawn from the bomb in specimens of the aqueous solution. The same tendency is assumed for ZnS although the writer knows of no other evidence to support the assumption. In the case of the tracer experiment, it is thought that no physical or chemical force was present which could have caused any particles to escape from the capsule. In general, however, because solid particles lack the thermodynamic properties characteristic of material in true solution, it seems probable that any free particles of solute would not disperse, but would remain in the vicinity of the dissolving solute, provided the sample was at the lowest point in the vessel and provided there was no bodily movement of the solution. It is perhaps worth noting that in experiments of this type, precipitation may be expected to occur wherever the solvent is at a lower temperature than the undissolved solute. Thus a connecting tube at a lower temperature than the bomb may accumulate radioactive material, provided there are no barriers to its migration from the bomb and provided there is somewhere for it to lodge.

CONCLUSIONS

A value of $.004 \pm .001$ gm/liter was obtained for the solubility of ZnS in H_2O at $130 \pm 5°$ C and at a pressure that varied between 4,000 and 5,000 psi during the experiment. The 25 percent maximum error is based on the distribution of readings obtained from repeated measurements of the same set-up. The error can be attributed about equally to the standardization measurements and to measurements made during the run. The precision of the method, as described here, could only have been established correctly by obtaining more solubility results at the same temperature and pressure; unfortunately electronic difficulties, and lack of time to correct them, prevented this.

The sensitivity and hence the precision of the method as described, would be improved by any arrangement which decreases the background radiation from all sources and increases the measurable radiation from the solution. This could be done by: a) Using a more radioactive sample. b) Using a larger detector crystal, or perhaps several crystals. c) Increasing the length and/or internal diameter of the bomb. d) Increasing the shielding round the crystal. By making the above improvements and by using suitable radiation equipment, it should be possible (with ZnS at a concentration of .004 gm/liter) to reduce the maximum error to two or three percent.

The information so far collected indicates that the assumptions upon which the method is based are sound and that radiation measurements can be interpreted in terms of solubility; however, the accuracy of the method has not yet been established for any sulfide. This could be done by comparing "tracer" results with results obtained by other methods, or by carefully analysing the liquid contents of the bomb after a solubility determination by the tracer method. The accuracy of the method described here could be improved by eliminating large temperature gradients in the bomb, and by reducing to a minimum any chemical link between the bomb chamber and the connecting tube. It is essential that tagged samples should be prepared

in such a way as to avoid chemical contamination or damage to the lattice structure. If temperatures above about 300° C are used, it will be necessary to modify the apparatus so as to ensure that the radiation counting equipment is not damaged by overheating.

The main feature of the tracer method is that a definite characteristic of the solution, closely related to solubility, can be measured without having to withdraw a sample and without having to alter the temperature or pressure in any way that might break the continuity of the experiment or introduce inaccuracies. This feature makes it possible to know when equilibrium between solid and liquid has been reached and so to establish a series of points on an equilibrium curve merely by changing temperature or pressure. In any study of this kind, much information on the rates of solution could be obtained.

The writer believes that the method can be used for studying a wide variety of solid-aqueous systems at any pressure and at any reasonable temperature assumed for hydrothermal processes.

ACKNOWLEDGMENTS

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Dec. 23, 1958

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THE GEOCHEMISTRY, ORIGIN, AND ROLE OF CARBON DIOXIDE, WATER, SULFUR, AND BORON IN THE YELLOWKNIFE GOLD DEPOSITS NORTHWEST TERRITORIES, CANADA[1]

R. W. BOYLE

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ABSTRACT

The gold deposits of the Yellowknife district occur in two distinct geological settings. The principal economic deposits occur in quartz-carbonate lenses in extensive chlorite schist zones (shear zones) cutting greenstone (amphibolite) rocks. The other deposits, of less economic importance, occur in quartz lenses in meta-sedimentary rocks.

The deposits in the greenstones represent concentrations of silica, carbon dioxide, water, sulfur, arsenic, antimony, gold, and other metallic elements. Those in the sediments represent concentrations of silica, sulfur, boron, gold, and other metallic elements.

For the deposits in the greenstones chemical evidence is presented to show that, under the influence of a strong thermal gradient, some of the carbon dioxide, water, sulfur, gold, silver, and other metallic elements in the original volcanic rocks was mobilized and migrated into the extensive shear zone systems. In the shear zones the chemical equilibrium was severely displaced, water and carbon dioxide reacted with the amphibolite rock producing extensive widths of chlorite and chlorite-carbonate schist, and silica, sulfur, gold, and numerous other elements present in the rock were mobilized. These mobilized constituents, together with those added by diffusion from the country rocks, migrated into dilatant zones, principally at shear zone junctions and flexures. In these sites they were precipitated as quartz, carbonates, sulfides, and gold.

A similar process has operated to form the gold-quartz lenses in the meta-sediments. In these rocks silica, boron, sulfur, and various metallic elements were mobilized during the metamorphism of the sediments, and these migrated into and were precipitated in dilatant zones in faults, fractures, and drag folds in the rocks.

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INTRODUCTION

THIS paper summarizes part of a research project carried out by the writer on the geochemistry and origin of the gold deposits of the Yellowknife district. A previous paper in this journal (4) outlined the geochemistry and suggested an origin of the major gold-bearing quartz veins in the greenstone belt of the district. The present paper adds further data on the geochemistry of the volatiles, offers an explanation for their present distribution, and discusses their role in the mineralization processes. A synthesis, summarizing the writer's views on the origin of the gold deposits, is given at the end of the paper.

It should perhaps be pointed out that another part of the project has dealt with the distribution and geochemistry of gold, silver, arsenic, antimony, copper, lead, and zinc in both the deposits and their host rocks. The results of this investigation are much too detailed to be described here, and the interested reader is referred to the writer's memoir (5) which will be published in the near future. Briefly the results indicate that the metals noted above are present in sufficient amounts in both the greenstones and sediments to provide the concentrations in the deposits. It has also been ascertained that the metals such as gold, silver, and zinc follow sulfur closely in their geochemistry, and hence statements made about the migration of sulfur in this paper also apply to these metals.

GENERAL GEOLOGY

The general geology of the Yellowknife district was described first by Stockwell and Kidd (19, 20) and later, in more detail, by Jolliffe (14, 15, 16, 17). More recently a description of the geology and a structural analysis of the principal ore-bearing shear zones of the greenstone belt was published by Henderson and Brown (12, 13). The geology of the orebodies of the Con-Rycon and Giant Mines was published by Campbell (7), Dadson and Bateman (10), Dadson (8, 9), Bateman (1), Brown and Dadson (6), and Boyle (2, 3). These authors have covered the geology of the district and gold deposits in considerable detail, and the brief description that follows gives a summary of the most important features and provides a background for discussing the part that the volatiles have played in the formation of the gold deposits.

The consolidated rocks within the area are Precambrian in age (Fig. 1). The oldest rocks are greenstones consisting of a succession of massive and pillowed andesite and basalt flows with interbedded dacite flows, tuffs, and agglomerates (Division A, Yellowknife Group). These rocks contain numerous gabbro and diorite sills and are cut by dikes of similar composition. Quartz-feldspar porphyry dikes and masses cut the greenstones throughout the district, but are found in greatest profusion in the northern part of the belt, particularly in the area east and southeast of Ryan Lake. The greenstones are overlain by a thick series of greywacke, argillite, slate, quartzite, and their metamorphic equivalents (Division B, Yellowknife Group).

Three large granitic masses occur within the district. One flanks the

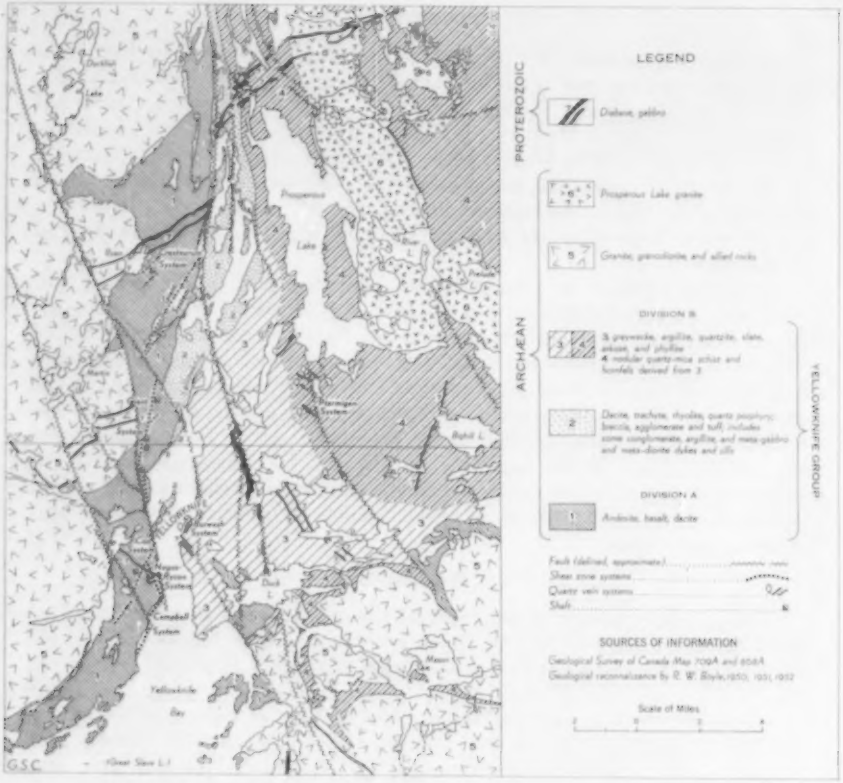
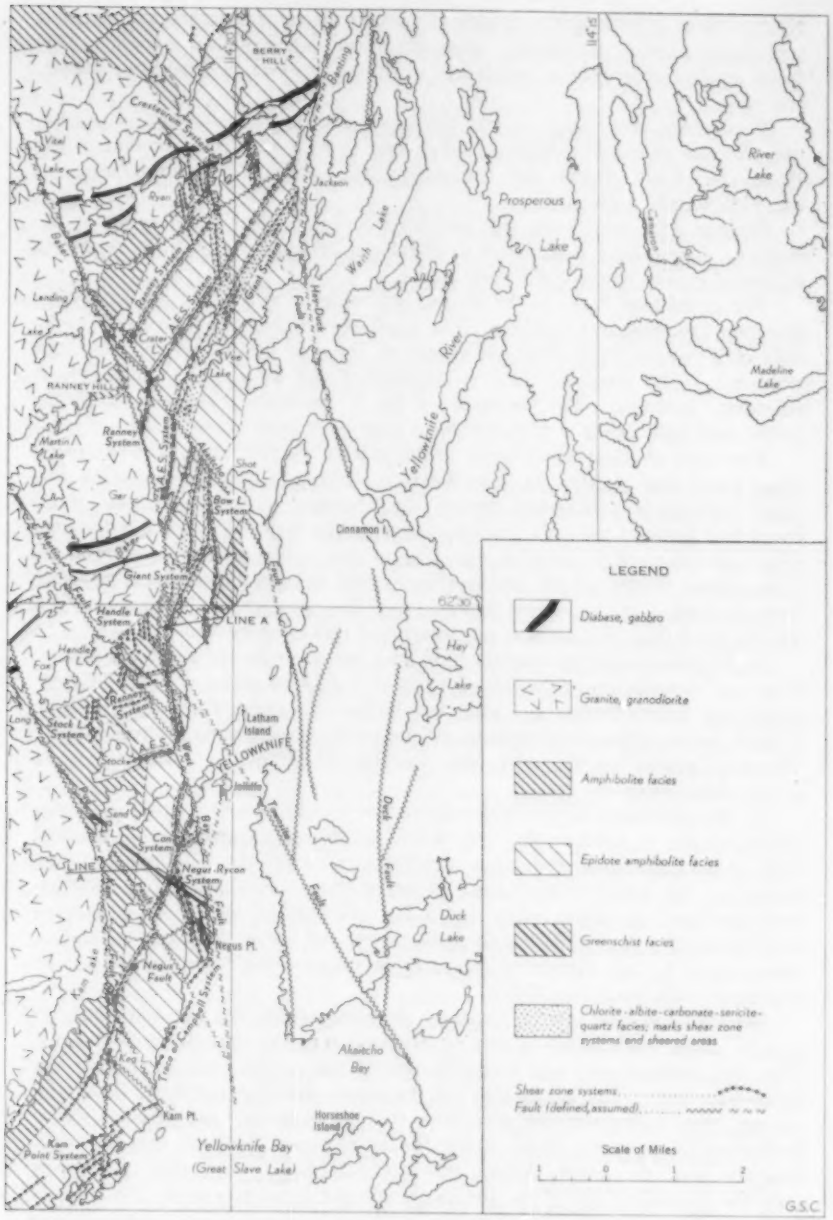


FIG. 1. Map showing general geology of Yellowknife District, Northwest Territories.

greenstone belt on the west, and another forms a large mass south of the sedimentary area. The third granitic mass, known as the Prosperous Lake granite, occurs east of Prosperous Lake. Field and chemical evidence suggest that the western granitic mass originated by granitization of a great series of sedimentary rocks lying stratigraphically below the greenstones. The Prosperous Lake granite and southeastern granitic mass were probably derived by granitization of parts of the Yellowknife sediments.

The greenstones have been extensively altered by regional metamorphism. The metamorphic facies (Fig. 2) are distinctly related to the granodiorite-greenstone contact and comprise a contact amphibolite facies, an intermediate epidote amphibolite facies, and a poorly developed greenschist facies.

Two metamorphic facies are clearly defined in the sediments and are related to the Prosperous Lake and southeastern granitic masses (Fig. 1).


LEGEND
Diabase, gabbro
Granite, granodiorite
Amphibolite facies
Epidote amphibolite facies
Greenschist facies
Chlorite-albite-carbonate-sericite-quartz facies; marks shear zone systems and sheared areas
Shear zone systems
Fault (defined, assumed)
Scale of Miles
1 0 1 2
G.S.C.
LINE A
YELLOWKNIFE
Latham Island
Prosperous Lake
River Lake
Madeline Lake
Yellowknife River
Cinnamon L.
Hay Lake
Duck Lake
Akaitcho Bay
Horseshoe Island
Kam Pt.
Negus Pt.
Yellowknife Bay
(Great Slave Lake)
RANNEY HILL
BERRY HILL
Ranney System
Giant System
Handle L. System
Negus-Rycon System
Kam Point System
Negus Fault
Kam Lake Fault
Duck Fault
Jackson-Campbell System
Welch Lake
Jackson L.
Ryan L.
Vivel Lake
Martin Lake
Gar L.
Shot L.
Bow L. System
Stock L. System
Sandy L.
Con System
Handle Fault
Long Fault
Ptarmigan Fault
Campbell Fault
Kam Lake Fault
Crestaurum System
Ryan Lake System
Cutter Lake System
Martin Lake System
Ranney System
Bow L. System
Stock L. System
Con System
Negus-Rycon System
Kam Point System
Jackson-Campbell System
Duck Fault
Campbell Fault
Ptarmigan Fault
Kam Lake Fault
Negus Fault
Handle Fault
Long Fault
Sandy L. Fault
Shot L. Fault
Gar L. Fault
Cutter Lake Fault
Vivel Lake Fault
Ryan Lake Fault
Crestaurum Fault
Jackson L. Fault
Welch Lake Fault
Hay Dyke
Yellowknife River

Next to these granitic masses a zone of nodular quartz-mica schist and hornfels containing garnet, andalusite, staurolite, and cordierite is present. This facies grades sharply into relatively unaltered greywacke, argillite, arkose. and slate.

Pegmatites, containing quartz, feldspar, mica, and locally typical pegmatite minerals such as tourmaline, beryl, and spodumene, are abundant in the Prosperous Lake granite and the quartz-mica schist and hornfels facies of the Yellowknife sediments.

Diabase dikes and basic sills are the youngest consolidated rocks in the district. These have a gabbroic to ultrabasic composition and are relatively unaltered except where cut by late faults.

The greenstone rocks of the district are folded into a broad northeasterly-plunging asymmetrical syncline. The northwest limb (greenstone belt) consists of a simple homoclinal succession of volcanic flows that dip and face southeast. The southeast limb is overturned and is in part folded into a subsidiary anticline. The sediments of the Yellowknife group are complexly folded into tight isoclinal folds which in turn have been cross-folded.

Two ages of shear zones occur in the greenstone belt (Fig. 2): (a) early shear zones that parallel the lava flows in strike and dip and contain a few small high-grade gold-quartz lenses, e.g., Ranney system, and, (b) shear zones that transect the lava flows and contain the large economic gold-quartz veins and lenses of the district, e.g., Con system. The Giant-Campbell shear zone system is the major ore-bearing system in the district and probably formed along a major thrust fault zone. The smaller but productive Con and Negus-Rycon systems are subsidiaries of this large system.

In the shear zone systems the principal ore controls are shear zone junctions and flexures and drag-folded parts of the large schist zones. The deposits are veins, lenses, and complex bodies of quartz that are generally marked by an adjacent carbonate-sericite-pyrite-arsenopyrite alteration halo. This halo grades imperceptibly into the chlorite-carbonate or chlorite schist of the shear zones.

In the sediments of the Yellowknife group gold-quartz veins and lenses are developed in small faults, drag folds, saddle reefs, ruptured and sheared axes of isoclinal folds, and other structures, all formed during the complex folding of the sedimentary rocks. Most of these veins and lenses have no well-developed alteration zones, but a few are marked by a narrow zone of tourmalinized rock. Structurally these veins and lenses are isolated bodies, unconnected to any system of fractures or faults along which hydrothermal solutions could have travelled.

Some of the gold-quartz lenses in the greenstones cut the last phase of granite dikes, from which it can be assumed that the deposits were formed after the emplacement and consolidation of the granitic mass flanking the greenstone belt. The lenses also cut the quartz-feldspar porphyry dikes and masses, thus ruling out the possibility that these bodies were the source of hydrothermal solutions from which the lenses were derived. In the sedimentary area the quartz lenses and veins appear to be contemporaneous with the metamorphism of the sediments and the formation of the Prosperous Lake granite.

Post-diabase faults and fractures cut all rocks in the district. In these faults quartz-hematite lenses and "giant quartz veins" are localized at or near junctions and flexures. Silicification, sericitization, and chloritization are the principal alteration effects in the rocks adjacent to the quartz bodies.

In the greenstones the principal minerals in the epigenetic deposits of the shear zones are quartz, carbonates, sericite, pyrite, arsenopyrite, stibnite, chalcopyrite, sphalerite, pyrrhotite, various sulphosalts, galena, scheelite, gold, and aurostibite. Two or more generations of quartz, carbonates, sulfides and gold are generally present in the complex orebodies. In the sediments the gold-quartz veins and lenses contain essentially quartz, with small amounts of pyrite, sphalerite, galena, tourmaline, and gold. Two or more generations of gold and quartz may be present in the veins.

The characteristic minerals in the late faults are quartz and hematite with small amounts of carbonates and chalcopyrite. Only traces of gold are found in the mineralized parts of the late faults.

GEOCHEMISTRY OF THE VOLATILES

A knowledge of the chemistry of the volatiles particularly water, carbon dioxide, sulfur, and boron is essential in any discussion of the origin of ore deposits. On the one hand are hydrothermalists who think that volatiles such as water and carbon dioxide are the transporting media for the ore and gangue elements. On the other are those who hold that the elements are concentrated by diffusion processes and that the volatiles act principally as catalysts and activating agents. It was with both these concepts in mind that the chemistry of water, carbon dioxide, sulfur, and boron, was traced in detail in the metamorphic facies, shear zones, and gold deposits.

All analyses for the volatiles were made on fresh material from outcrops and mine workings. Composite samples from the various facies were employed for the most part, but samples on traverses across the metamorphic facies were used to trace the migration of water, carbon dioxide, and sulfur, e.g., Line A, Fig. 2.

Water, Carbon Dioxide, and Sulfur.—In the rocks, in their present state, most of the water is bound in amphiboles, chlorite, and the mica minerals. Small amounts also occur along grain boundaries and in liquid inclusions in all minerals. Carbon dioxide is fixed mainly in the carbonates, but small amounts are present in apatite and other minerals, along grain boundaries, and in liquid inclusions. Sulfur is held principally in the sulfides with only small amounts in apatite and in the sulfates of liquid inclusions. Table 1 records the contents of water, carbon dioxide, and sulfur, in the metamorphic facies, shear zones, and quartz lenses of the greenstone belt and sedimentary area. Figure 3 gives a graphical representation of the generalized analytical results from the greenstone belt. Attention is called to the following features:

In the greenstone belt the contents of water, carbon dioxide, and sulfur increase toward the lower grade facies, i.e., outwards from the granodiorite. In the sedimentary area water is the only volatile that shows any significant change across the metamorphic facies. As in the greenstone belt there is an increase in the content toward the lower grade facies.

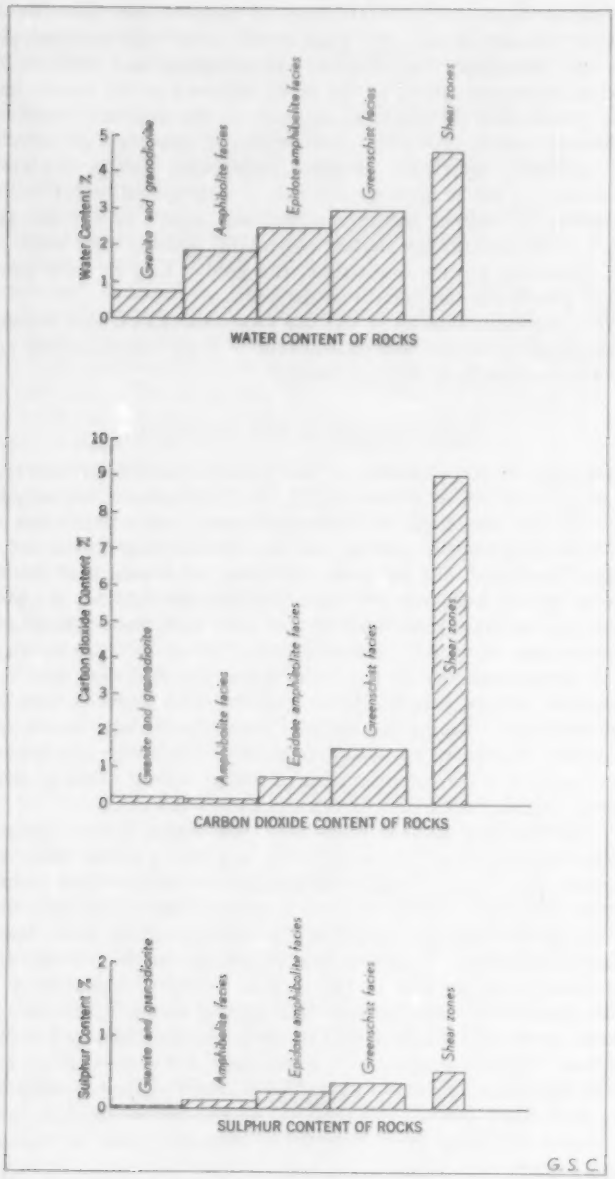


FIG. 3. Water, carbon-dioxide, and sulfur content of granitic rocks, metamorphic facies, and shear zones, Yellowknife greenstone belt, Northwest Territories.

TABLE 1

CONTENT OF VOLATILES (H_2O, CO_2, S) IN ROCKS OF THE YELLOWKNIFE DISTRICT

Description of rock and facies	H_2O (total), wt. %	CO_2, wt. %	S, %	Remarks
Greenstone Belt				
Western granodiorite	0.75	0.14	0.03	Average values calculated from analyses of composite samples
Amphibolite facies	1.84	0.09	0.09	Average values calculated from analyses of composite samples
Epidote amphibolite facies	2.47	0.68	0.20	Average values calculated from analyses of composite samples
Greenschist facies	3.00	1.28	0.20	Average values calculated from analyses of composite samples
Tuffs and other sediments	1.56	5.55	1.45	Analysis of composite sample of graphitic tuff
Chlorite-carbonate schist in shear zones	5.33	8.03	0.12	Composite sample
Carbonate-sericite schist in shear zones	1.26	15.57	3.26	Composite sample
Quartz-carbonate lenses and veins	0.50	4.00	2.30	Contents variable; approximations only
Sedimentary Area				
Prosperous Lake granite	0.43	0.18	Trace	Average values calculated from analyses of composite samples
Knotted quartz-mica schist and hornfels	2.38	0.12	0.13	Average values calculated from analyses of composite samples
Relatively unaltered slate, phyllite, greywacke, and argillite	3.35	0.07	0.12	Average values calculated from analyses of composite samples
Pegmatites	0.50	0.10	Trace	Average values calculated from analyses of composite samples
Quartz veins	0.50	0.10	0.50	Contents variable; approximations only

Analyses by J. A. Maxwell, R. J. C. Fabry, S. Courville, and R. W. Boyle.

The shear zones cutting the greenstones show a marked enrichment in water, carbon dioxide, and sulfur, and the quartz-carbonate bodies in the shear zones are enriched in carbon dioxide and sulfur. The pegmatites cutting the sediments exhibit no enrichment in the volatiles nor are they surrounded by hydrous or carbonated zones. The quartz veins in the sediments are likewise not enriched in water or carbon dioxide, but locally they may have higher than average amounts of sulfur.

The profiles of water, carbon dioxide, and sulfur are instructive in determining the trend of migration of these compounds and their probable source. Ideally the profiles along traverse lines rise toward the lower grade facies and simulate diffusion profiles (Fig. 4 (a)). They are best explained by the mobilization of volatiles initially present in the rock followed by diffusion away from a high temperature zone, i.e., diffusion down a thermal gradient. If the granitic rocks were the source of the volatiles the profiles should simulate the one shown in Figure 4 (*b*). That is, the greatest concentration of volatiles should exist in the rocks adjacent to the source, and the content of volatiles should decrease with distance from the source.

It might be argued, however, that when the granitic rocks produced the

volatiles (i.e., during their last stages of crystallization) the adjacent greenstone rocks were so highly heated that the volatiles were carried well out of the contact zones. Here one must carefully note certain phase relationships between the granitic rocks and the amphibolite facies of the greenstones. Muscovite and chlorite are present in the last phases of the western granitic mass. These minerals are also present in the greenschist facies and in the shear zones where the volatile content is high. From thermodynamic considerations it follows that since muscovite and chlorite were stable minerals when the granite formed they would also have been stable in the adjacent amphibolite facies if the necessary amount of water had been available. Muscovite and chlorite are, however, not prevalent minerals in the amphibolite facies and the inference is, therefore, clear that large amounts of water and

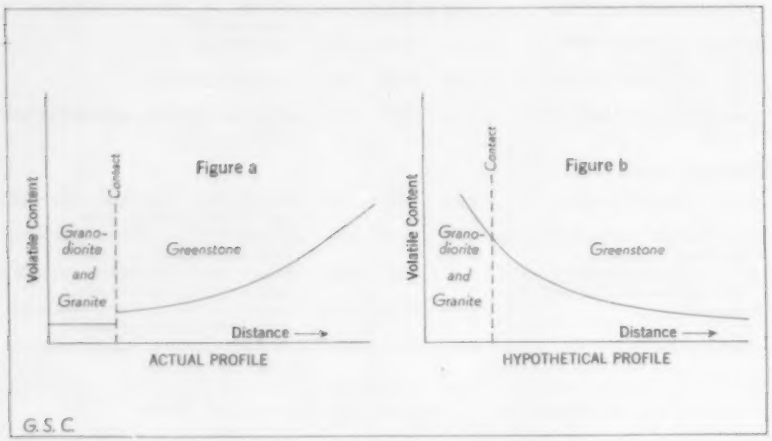


FIG. 4. Comparison of actual and hypothetical profiles of volatile contents of greenstone rocks.

carbon dioxide were not given off by the granite and added to the adjacent amphibolite zone. If the volatiles had migrated in quantity into the greenstone rocks adjacent to the granite, extensive carbonated, sericitized, and chloritized zones would have been developed, and large concentrations of sulfides could be expected.

In the sedimentary rocks similar features are present. There are no hydrated, carbonated, or sulfurized zones adjacent to the Prosperous Lake granite. On the contrary, the rocks in the knotted quartz-mica schist zone adjacent to the granite are dehydrated having lost more than one percent of their water when compared with the average water content of a normal sedimentary series of shale, argillite, and greywacke.[2]

[2] The average water content of a normal sedimentary series of shale, argillite, and greywacke, as compiled from various sources, lies close to 3.5%. R. A. Daly (Igneous rocks and the depths of the earth, McGraw-Hill Book Company, New York, 1933, p. 478), gives 1.64% H_2O as an average for sandstones and 5.02% H_2O for shales.

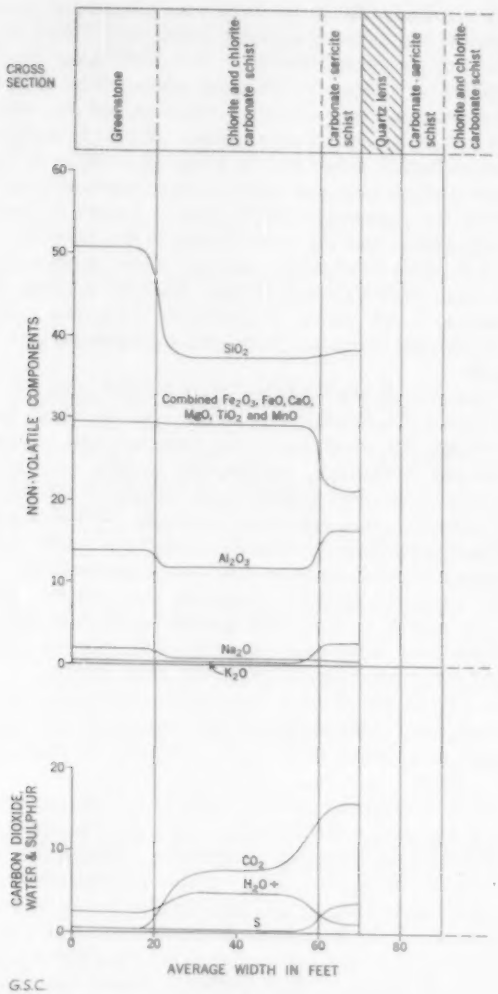


FIG. 5. Chemical changes produced by alteration of greenstone. Composite samples from all shear zones.

Space does not permit a detailed discussion of the role of carbon dioxide, water, and sulfur in the formation of the shear zones and gold-quartz bodies in the greenstone belt. For this the interested reader is referred to a previous paper by the writer (4). Only the more important features are described here.

Table 2 records analyses of composite samples of greenstone, chlorite-carbonate schist, and carbonate-sericite schist, and Figure 5 gives a graphical representation of the chemical changes that have taken place during the formation of gold-quartz lenses in the shear zones. The main points of interest are the consistent increase in carbon dioxide and the marked decrease in silica as the quartz bodies are approached. Water is enriched in the chlorite and chlorite-carbonate phase and is lower in content in the sericite phase. Sulfur shows a slight decrease in the chlorite-carbonate schist and a marked enrichment in the carbonate-sericite phase. Potash is enriched in the carbonate-sericite phase, and the soda content is decreased in both the chlorite-carbonate and carbonate-sericite phases. Iron, magnesium, calcium, and manganese show individual trends, but the total content of their combined oxides decreases in all phases of alteration. Alumina exhibits a slight decrease in the chlorite-carbonate phase and a substantial gain in the carbonate-sericite phase.

These changes in the chemical constituents represent a trend toward equilibrium in the shear zones. As carbon dioxide, water, and sulfur diffused into and through the shear zones, the feldspars and cafemic minerals were attacked, chlorite, carbonates, sericite, and sulfides were formed at their expense, and large quantities of silica were released. These introductions and subsequent reactions were promoted principally by the dilatancy of the shear zones. Where structural movement along the shear zones created low pressure zones the physiochemical equilibrium was re-established by the lateral and upward migration of silica into these zones where this constituent was precipated as quartz to form the quartz bodies. Similar equilibrium adjustments have lead to the rearrangement of the cafemic oxides, soda, potash, alumina, and other constituents within the shear zones.

Boron.—The results of a spectrographic investigation of the boron content of the various rock types at Yellowknife, together with average analyses of similar unmetamorphosed rock types are given in Table 3. The following points are evident.

The sedimentary rocks contain much higher contents of boron than the basic volcanic and dike rocks, a feature that is also shown by the average boron contents of similar unmetamorphosed rocks. Hence, one can conclude that the differences in the boron contents of the Yellowknife rocks were inherited when the rocks were formed and are not the result of later additions from magmatic solutions. It should also be pointed out that there is no noticeable enrichment of boron in the high-grade facies of either the greenstone belt or sedimentary area, a feature that further indicates that the granites did not supply the boron. Similar conclusions were reached by Goldschmidt (11) as a result of his research on boron in rocks.

The shear zones and quartz veins in the greenstone rocks (average boron content, < 10 ppm), are markedly low in boron, whereas the quartz veins and pegmatites in the knotted schist aureole (average boron content, 70 ppm) of the Prosperous Lake granite are enriched in boron. The pegmatites in the Prosperous Lake granite (average boron content, 170 ppm) carry significant concentrations of boron held in tourmaline whereas those present in

TABLE 2

CHEMICAL CHANGES PRODUCED BY ALTERATION OF GREENSTONE, COMPOSITE SAMPLES OF ALL SHEAR ZONE SYSTEMS

	A-76, %	A-251, %	Adjusted, %	Gains and losses in constituents	Percentage gains and losses	A-250, %	Adjusted, %	Gains and losses in constituents compared with A-76	Percentage gains and losses
SiO_2	50.45	40.36	37.12	−13.33	− 26.42	38.19	38.30	−12.15	− 24.08
Al_2O_3	13.96	12.87	11.84	− 2.12	− 15.19	16.26	16.31	+ 2.35	+ 16.83
Fe_2O_3	2.00	1.06	0.97	− 1.03	− 51.50	0.38	0.38	− 1.62	− 81.00
FeO	9.61	12.00	11.04	+ 1.43	+ 14.88	3.49	3.50	− 6.11	− 63.58
CaO	10.23	8.94	8.22	− 2.01	− 19.65	11.02	11.05	+ 0.82	+ 8.02
MgO	6.53	8.43	7.75	+ 1.22	+ 18.68	5.77	5.79	− 0.74	− 11.33
Na_2O	1.85	0.90	0.83	− 1.02	− 55.14	0.29	0.29	− 1.56	− 84.32
K_2O	0.39	0.41	0.38	− 0.01	− 2.56	2.82	2.83	+ 2.44	+ 622.64
H_2O+	2.36	5.20	4.78	+ 2.42	+102.54	1.16	1.16	− 1.20	− 50.85
H_2O-	0.11	0.13	0.12	+ 0.01	+ 9.09	0.10	0.10	− 0.01	− 9.09
TiO_2	1.02	1.05	0.97	− 0.05	− 4.90	0.82	0.82	− 0.20	− 19.61
P_2O_5	0.13	0.11	0.10	− 0.03	− 23.08	0.21	0.21	+ 0.08	+ 61.54
MnO	0.21	0.22	0.20	− 0.01	− 4.76	0.17	0.17	− 0.04	− 19.05
CO_2	0.68	8.03	7.39	+ 6.71	+986.76	15.57	15.62	+14.94	+2,197.06
S	0.22	0.12	0.11	− 0.11	− 50.00	3.26	3.27	+ 3.05	+1,386.36
Cl	0.02	0.00	0.00	− 0.02	−100.00	0.01	0.01	− 0.01	− 50.00
Cr_2O_3	0.03	0.03	0.03	0.00	0.00	0.00	0.00	− 0.03	− 100.00
C	0.04	0.12	0.11	+ 0.07	+175.00	0.04	0.04	0.00	0.00
As_2O_3						1.50	1.50		
Total	99.84	99.98				101.06			
Less O = S, Cl	0.10	0.05				1.22			
Net total	99.74	99.93				99.84			
Specific gravity	2.99	2.75				3.00			
Analyst	J. A. Maxwell	S. Courville				S. Courville			

Notes:

1. A-76—Composite sample of epidote amphibolite facies (greenstone).
2. A-251—Composite sample of chlorite-carbonate schist of shear zones.
3. A-250—Composite sample of carbonate-sericite schist of shear zones.
4. Adjusted % = percentages of A-251 and A-250 multiplied by the factors 2.75/2.99 and 3.00/2.99, respectively, to reduce to a common volume.

TABLE 3

BORON CONTENT OF THE ROCKS OF THE YELLOWKNIFE DISTRICT COMPARED WITH GEOCHEMICAL AVERAGES OF SIMILAR UNMETAMORPHOSED ROCK TYPES

Yellowknife District, rock types, facies, etc.	B, (ppm) (1)	Similar rock types (2)	Geochemical average B, (ppm)
Greenstone belt			
Western granodiorite, composite	20–40	Granites	0.9–3
Amphibolite facies	<10	Basalts and gabbros	1.6–3
Epidote amphibolite facies	<10		
Greenschist facies	<10		
Meta-diorite and gabbro dikes	<10		
Shear zones	<10		
Tuffs	10–100		
Sedimentary area			
Prosperous Lake granite and pegmatites, composite	200–600		
Prosperous Lake granite	40–300	Granites	0.9–3
Pegmatites	1,000–2,000		
Knotted quartz-mica schist and hornfels	40–100	Shales	310
Relatively unaltered argillite, graywacke, slate, etc.	50–100	Quartzites	9–31
Quartz-feldspar porphyry	20–60		
Diabase dikes	<10	Basalts and gabbros	1.6–3

Notes:
(1) Analyses by spectrographic laboratory, Geological Survey of Canada.
(2) Data from Rankama, K., and Sahama Th. G.—Geochemistry, University of Chicago Press, 1949.

the western granodiorite (average boron content 30 ppm) contain little or no tourmaline. From the foregoing it is clear that where quartz bodies and pegmatites cut rocks containing an ample supply of boron they are enriched in this element, and the obvious inference is that the host rocks have provided the boron. If the boron were derived from magmatic hydrothermal solutions it is most difficult to account for these differential concentrations on any physiochemical basis.

Discussion.—There is no need to call upon granitic differentiation processes for any of the volatiles in the rocks, shear zones, quartz bodies, or pegmatites, in the Yellowknife district. On the contrary the facts suggest that initially sufficient quantities of the volatiles were normal components of the country rocks.

Considering the greenstones it is logical to assume that prior to metamorphic reconstitution they would contain one-half of one percent water (average for basalts). Sulfur and carbon dioxide would likewise be initial constituents. Many of the greenstones are amygdalar indicating a considerable initial volcanic gas content (H_2O, HCl, CO_2, H_2S, SO_2 etc.). The boron content would be low judging from the geochemical averages of basic rocks. Furthermore, it should be borne in mind that the greenstones were laid down on the ocean floor as suggested by the presence of pillows and

interbedded tuffs. During their deposition, consolidation, and cooling they would absorb and trap sea water containing various other volatiles. As a grand total, therefore, it can be logically assumed that the initial concentration of volatiles in the greenstones would be sufficient to produce any of the metamorphic effects in the rocks and the alteration of the shear zones.

As for the sediments it is well known that shales, argillites, etc., contain an abundance of water both in their constituent minerals and in interstices. Sulfur and carbon dioxide are also normal original constituents of sediments and are commonly present in considerable concentrations. Boron would be initially present in the tourmaline of the resistates and also as adsorbed ions.

On quantitative grounds some may question the postulate that the host rocks were the source of the sulfur and metallic elements in the deposits. There seems to be little justification for this criticism when one considers the facts on the provenance of these elements. In Table 4 are given total amounts of S, As, Sb, Cu, Zn, Au, and Ag in the rock of the Giant-Campbell system prior to shearing and the amounts of these elements in the deposits. The ratio of concentration is also given as a percentage. For calculation the dimensions of the system were taken as follows: length—10 miles, average width —500 feet, depth—3 miles. The contents of the elements in this amount of rock, as averaged from spectrographic and chemical analyses of unsheared greenstone rocks, were taken as follows: S—1,500 ppm, As—12 ppm, Sb—1 ppm, Cu—50 ppm, Zn—50 ppm, Au—0.01 ppm and Ag—1 ppm. The amount of ore in the system was assumed to be 6 million tons, twice the amount mined and in known reserves. The tenor of this ore, as averaged from the analyses of the ores in the greenstone belt, was taken as follows: S—2.34%, As—1.35%, Sb—0.15%, Cu—0.07%, Zn—0.28%, Au—0.654 ounce/ton, and Ag—0.139 ounce/ton.

The author is fully aware that many factors enter into calculations such as those given in Table 4. However, he feels that while the figures are not exact they at least give the order of magnitude. It is apparent from these figures that all sulfur, arsenic, antimony, and other chalcophile elements could have been derived solely from the sheared rock of the shear zone. When one considers the probable contribution of gold, silver, and the sulfide con-

TABLE 4

CONTENTS OF CHALCOPHILE ELEMENTS IN SHEAR ZONES AND DEPOSITS OF THE GIANT-CAMPBELL SYSTEM

Element	Total content in shear system prior to shearing and alteration (millions of tons)	Total content in deposits (millions of tons)	Ratio of concentration, %
S	62	0.14	0.226
As	0.5	0.081	16.2
Sb	0.04	0.009	22.5
Cu	2.0	0.004	0.20
Zn	2.0	0.017	0.85
Au	12.2×10^6 (ozs.)	3.9×10^6 (ozs.)	32.0
Ag	$1,219 \times 10^6$ (ozs.)	0.834×10^6 (ozs.)	0.068

stituents to the shear zones during the metamorphism of the greenstone belt as a whole there is little need to call upon outside sources such as magmatic solutions to supply these elements. The same can also be said for deposits in the sediments.

The present distribution of the volatiles in the metamorphic facies and shear zones in the greenstones and in the metamorphic facies in the sediments is best explained by the mobilization, migration, and concentration of the volatiles initially present in the rocks. The migration of the volatiles has taken place under the influence of a thermal gradient, and equilibrium among the components of the rocks in the presence of differing concentrations of volatiles has been attained by the formation of characteristic mineral phases that enable one to map the metamorphic facies. In the shear zones equilibrium has been established by the migration of silica into dilatant zones to form the quartz bodies and by the rearrangement of numerous other constituents. Similar chemical adjustments during metamorphism have given rise to the quartz lenses in the sedimentary rocks.

In the country rocks and shear zones the effects of the volatiles are manifest over great distances, and alteration of the rocks and minerals has taken place in the minutest detail. Such pervasive chemical effects can hardly be attributed to the action of solutions percolating along fractures. Rather, diffusion processes seem more capable of producing such extensive alteration effects and giving the characteristic profiles across the shear zones and metamorphic facies. Considering the deep seated conditions under which the gold-quartz lenses were formed one is led to the conclusion that ionic or gaseous diffusion along grain boundaries and other discontinuities in the minerals and rocks was the effective mechanism by which both the volatiles and metals migrated.

If one accepts the migration of elements in rocks by diffusion, water no longer plays its classical role as a transporting agent in the hydrodynamical sense. Instead this volatile acts mainly as a catalyst and activating agent which promotes the mobilization and migration of many constituents. The writer is of the opinion that large volumes of flowing water are unnecessary for the formation of veins and lodes of the deep-seated Yellowknife type. A more adequate explanation of the role of water would seem to be that this volatile formed a pervasive gaseous medium through which the various ions migrated. This view can be supported by the recent researches of Morey (18) who has shown that numerous oxides, including silica, are relatively soluble in gaseous water, and by the observations of many chemists that ions migrate readily through a gaseous water medium.

In the writer's view the role of water in the formation of the Yellowknife deposits has been, therefore, largely that of a catalyst. In addition this volatile in consort with carbon dioxide and sulfur has acted as an activating agent in liberating large amounts of silica that was delivered to dilatant zones in the shear zones of the greenstones. In this role the three volatiles have also bound many elements forming the characteristic minerals of the shear zones and alteration halos.

SYNTHESIS OF MINERALIZATION PROCESSES

The role of the volatiles and the origin of the gold-quartz deposits at Yellowknife can best be illustrated by the following historical synthesis of the mineralization of the greenstone belt and sedimentary rocks. Figure 6 is a schematic representation of the synthesis as it applies to the greenstone belt.

In early Precambrian time a thick series of marine sediments was laid down followed by extensive extrusions of lava flows that now form the greenstone belt. This was followed by further deposition of marine sediments (Yellowknife group).

A period of great orogeny followed during which the competent lavas were folded into a broad syncline, and the less competent sediments were complexly folded. Near the end of the orogenic period the sediments lying below the greenstones were granitized to form the western granitic mass. Large zones of the sediments lying above the greenstones (Yellowknife group) were also granitized to form the Prosperous Lake and southeastern granitic masses.

During these orogenic processes a strong temperature gradient existed outward from the foci of granitization leading to the formation of the zone facies of metamorphism in the greenstone belt and sedimentary rocks. At this time much water, carbon dioxide, sulfur, and some of the chalcophile elements including gold and silver, were mobilized in the greenstone belt and migrated toward the cooler parts, that is, down the temperature gradient at right angles to the isothermal lines as shown by the vectors in Figure 6 (a). If there had been no structural breaks in the rocks the result would have been a simple metamorphic halo about a granitized centre.

However, in the greenstone belt a great system of shear zones was formed near the end of the orogeny, after the consolidation of the granitic bodies. As a consequence the migration vectors were radically changed by the dilatancy of the shear zones as shown in Figure 6 (b). The shear zones literally sucked the mobile carbon dioxide, water, sulfur, and other elements from the country rocks and funnelleled them toward the surface. Because of the great extent and depth of the shear zones the effects of dilatancy were undoubtedly felt over a great volume of the country rocks, and mobile elements were probably contributed from points thousands of feet horizontally and vertically from the shear zone systems. Extensive structures that impose such marked dilatant effects on the country rocks may be termed "first degree dilatant zones."

During the formation of the large shear zones carbon dioxide, water, and sulfur reached a high concentration along them. As a consequence the chemical equilibrium was strongly displaced, and chloritization, carbonatization, and pyritization, of an enormous tonnage of volcanic rock too place. This led to the liberation of silica, potassium, calcium, iron, etc., and in addition gold, silver and other metallic elements present in the rock affected by alteration. These liberated compounds and elements, together with those added to the shear zones by diffusion from the host rocks, migrated laterally and vertically to "second degree" low pressure dilatant zones at shear zone junctions and other structural locales where contorted zones or openings were

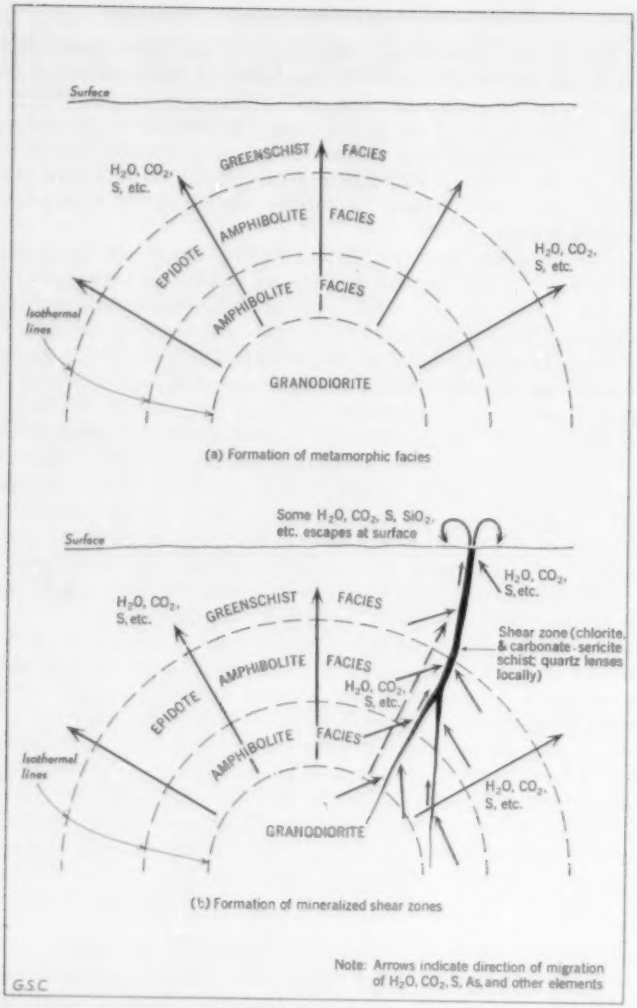


FIG. 6. Schematic diagrams to illustrate the formation of metamorphic facies and mineralized shear zones in the greenstone belt.

formed. In these sites, secondary reactions promoted by low pressure and lower chemical potential resulted in the precipitation of quartz, carbonates, pyrite, arsenopyrite, and gold, forming quartz-sulphide-gold lenses with adjacent alteration halos.

In the sedimentary rocks the quartz lenses and their contained sulfides

and gold were concentrated by similar processes. During severe structural deformation of the rocks many dilatant zones appeared in drag-folded parts of the beds, along faults, and along sheared axes of anticlines and synclines. To restore the chemical equilibrium within the rocks silica, sulfur, boron, and various metallic elements migrated into these zones where they were precipitated, forming the gold-quartz-sulfide veins and lenses. The mobilization and migration of the compounds and elements forming the gangue and ore minerals were promoted principally by the high temperature and stress that prevailed during the metamorphic processes.

In late Precambrian time all rocks were extensively faulted, and this was followed by deposition of quartz and hematite at certain favorable sites in the late faults. The agents of regional metamorphism were not active at this time and only the highly mobile compound, water, played a major part in the limited mineralization. The water attacked the various minerals in the fault breccia and adjacent wall rocks reducing them to chlorite and sericite. Silica was liberated together with iron and a few other elements. The silica and iron migrated into dilatant zones along the faults where they were precipitated as quartz and hematite. The presence of hematite emphasizes the high oxidation potential present when the mineral was formed. If carbon dioxide and sulfur had been mobilized, as was the case during the formation of the shear zones, extensive bodies of carbonates and sulfides would have been formed in the late faults.

CONCLUSIONS

The detailed research on the origin of the gold-quartz deposits of the Yellowknife district suggests the following:

1. The volatiles and other constituents of the deposits were derived by lateral and vertical secretion from the series of rocks in which they occur.

2. The energy necessary to mobilize various elements and concentrate them in deposits was in part inherent in the metamorphic processes and in part due to dilatancy resulting from structural deformation.

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OTTAWA,
Jan. 22, 1959

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GEOLOGY OF THE MONTGARY PEGMATITE

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ABSTRACT

The Montgary pegmatite is located at Bernic Lake in the southeastern Manitoba pegmatite district. It has a complex internal structure with several contrasting mineral assemblages. The pegmatite contains a number of potentially valuable minerals including spodumene, amblygonite, lepidolite, zinnwaldite, pollucite and beryl. The distribution of each of these within the pegmatite is related to the internal structure and controlled by a specific mineral assemblage. Parts of the pegmatite contain a high concentration of spodumene. The pollucite occurrence is of unique character and is one of the largest known deposits of this mineral.

The pegmatite is sill-like in attitude with a maximum dip of about 15 degrees. Its contacts with the amphibolitic wall rocks are sharp and tourmalinized.

Mineral assemblages present include perthite-plagioclase-quartz-muscovite, spodumene-microcline perthite-plagioclase-quartz-muscovite, cleavelandite-lithia micas-quartz, quartz amblygonite, albite, lepidolite, pollucite, and quartz assemblages. The occurrence and relationships of these are

described and possible relationships between attitude and internal structure are discussed.

Many features of the pegmatite suggest that the deposit formed by crystallization and differentiation of a pegmatite fluid in a restricted system. These features are discussed. The nature and occurrence of the pollucite, lepidolite and albite assemblages are such, however, that it is difficult to visualize them resulting from such a system. These assemblages may be of later replacement origin. The source of the late, alkali-rich replacing solutions may be unmixing of soda and the rarer alkalis (lithium, rubidium, caesium) from earlier-formed silicates in a manner analogous to the unmixing of soda feldspar in perthites. Various aspects of this hypothesis are examined.

INTRODUCTION

The Montgary pegmatite is located at Bernic Lake in the southeastern Manitoba pegmatite district (Fig. 1). It lies about 110 miles by road northeast of Winnipeg.

LOCATION MAP — FIG. 1

History—The present Montgary property was first explored for cassiterite in the late 1920's. Diamond drilling was carried out, a shaft was sunk to about 120 feet and a limited amount of underground development work was completed by Jack Nutt Tin Mines on shallow cassiterite-bearing pegmatites. A single drill hole penetrated a thick pegmatite at depth that proved to contain spodumene. Work on the cassiterite deposits ceased in 1930.

No further work was done on the property for some years. Finally in 1954, due to increasing interest in lithium, the property was re-staked by Montgary Explorations Limited, and a program of diamond drilling was carried out to test the deeper spodumene-bearing pegmatite. As a result plans were completed for installation of a mining plant, and a shaft was collared in

late 1956. Shaft sinking was carried out by Montgary Explorations Limited during the summer and fall of 1957, to a depth of 320 feet, and a station was cut at 280 feet, but work ceased in November, 1957.

This work, together with additional drilling by the American Metal Company Ltd. (now American Metal Climax Inc.) in March, 1957, outlined the extent of the spodumene deposit and indicated that interesting amounts of pollucite, lepidolite, amblygonite and beryl were present.

Acknowledgments.—All of the recent work on the property has been carried out by Montgary Explorations Ltd. and by the American Metal Company Limited, and the permission of both these companies to publish the data given here is gratefully acknowledged.

Thanks are due to Mr. G. A. McCartney, Mr. Frank James and Mr. Frank Brown of Montgary Explorations Ltd. for their cooperation in making available all of that company's facilities. Mr. H. T. Leslie, consulting engineer for Montgary, provided much valuable information regarding the earlier Montgary work. Credit is also due to numerous members of the American Metal Co. staff for their parts in carrying out that company's program. This was under the supervision of Mr. Roy Jure, drilling at the property was in charge of Mr. L. O. Ostensoe, and Mr. R. Berube prepared many plans and sections.

The writer is indebted to Dr. W. W. Moorehouse and Dr. P. A. Peach of the Geology Department at the University of Toronto for their assistance in regard to bibliographic and laboratory phases of the work. Dr. E. N. Cameron and Dr. S. W. Bailey of the Geology Department at the University of Wisconsin, and Dr. J. A. James of the American Metal Co. gave helpful advice and criticism during the preparation of this paper.

GENERAL GEOLOGY

The general geology of the Bernic Lake area has been described by a number of writers, most recently by Springer (9) and Davies (3). The surface geology of the Montgary property is shown in detail on Manitoba Department of Mines Map 54-1 by Davies (3).

The country rock consists chiefly of a massive hornblende-plagioclase gneiss or amphibolite. The amphibolite trends east–west and dips vertically or steeply to the south. At the northwest extremity of Bernic Lake the amphibolite lies in contact with a massive, pink granite that apparently intrudes it. The amphibolite has also been intruded by many pegmatite dikes and sills, some of which contain cassiterite and beryl together with several lithium and other rare-element minerals.

EXTERNAL STRUCTURE, WALL ROCK CONTACTS, WALL ROCK RELATIONSHIPS

The Montgary pegmatite is a sill-like body having a low angle of dip. True strike and dip are therefore difficult to determine, but the pegmatite appears to strike in a northwesterly direction and to have a maximum dip of about 15° NNE. The sill ranges from 60 to 200 feet in thickness and is roughly circular in plan with a diameter of about 1,500 feet (Fig. 2).

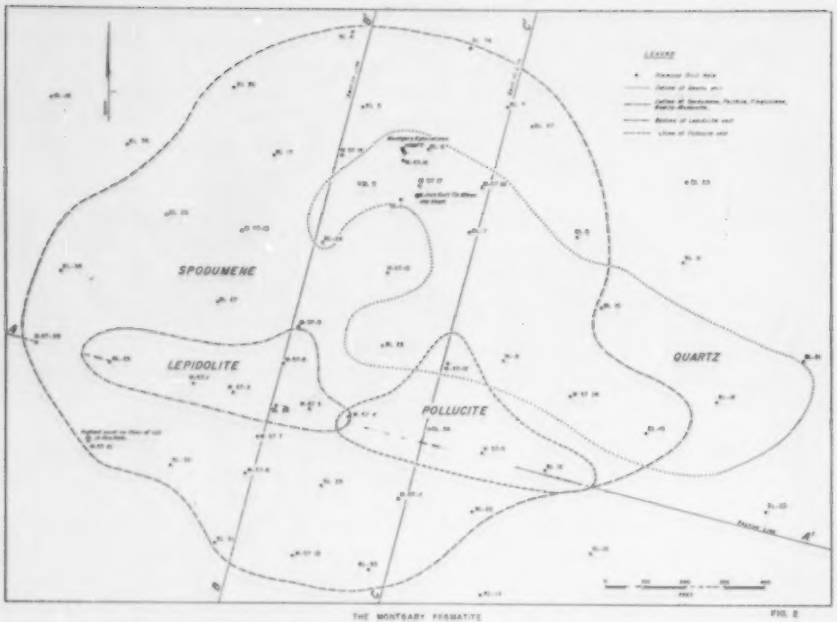

FIG. 2. Plan map showing locations of diamond drill holes, horizontal projection of certain mineral assemblages and lines of sections.

The highest point or apex of the sill lies in the bed of Bernic Lake (Fig. 2) and this is the only point where the pegmatite reaches the bed rock surface. From this apex the sill appears to dip gently in all directions to the north, northeast and east with a maximum dip to the north-northeast. Thus the upper contact of the sill seems to be shaped like an inverted saucer.

The nature of the upper and lower contacts of the sill is not known. Drill holes show that the contacts are sharp, the upper more so than the lower, and the wall rock is commonly tourmalinized for a width of a few inches along the contact. Thin sections show that hornblende of the wall rock immediately at the contact is largely altered to biotite. Other than this there appears to have been very little reaction between the wall rocks and the pegmatite.

The upper contact is exposed at a vertical depth of about 229 feet in the Montgary Explorations Ltd. shaft. Here again the contact is very sharp (Fig. 3) and the wall rock is tourmalinized. The contact is not planar but gently rolling; there is one pronounced upward bulge.

In several drill holes short intersections (1–3 feet) of fine-grained, dark rock were cut within the pegmatite. In all cases this rock is in sharp contact with pegmatite and is generally more or less tourmalinized. In most cases crystal growth in the pegmatite is oriented perpendicular to the contact

and appears to have proceeded outward from it. Most of these sections of dark rocks are believed to be altered inclusions of the amphibolitic wall rocks. It is possible, however, that some may be late lamprophyre dikes cutting the pegmatite.

Several small, angular wall-rock inclusions are exposed in the southeast face of the shaft station at 282 feet (Fig. 4). These are also tourmalinized and each is rimmed by a narrow $\frac{1}{2}$-inch band of plagioclase beyond which spodumene-bearing pegmatite is present. The plagioclase rims appear to

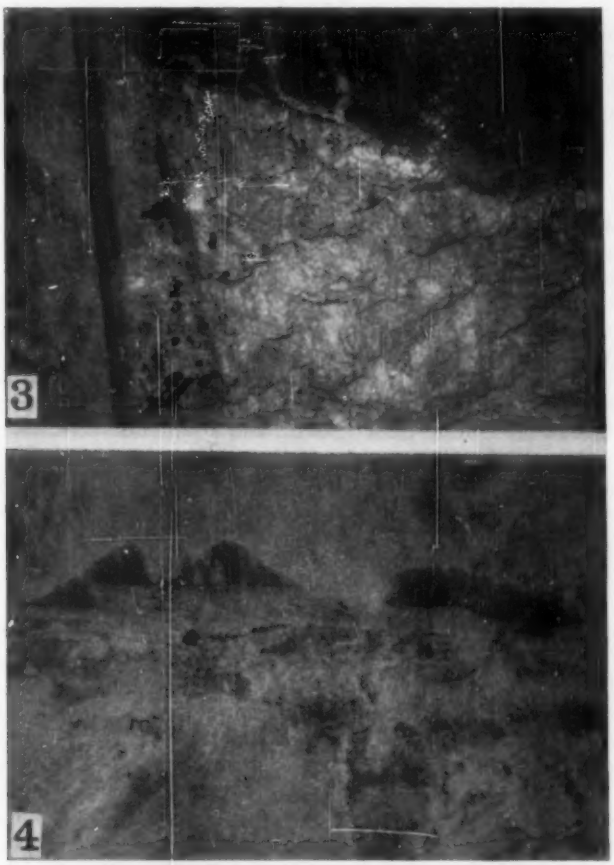

FIG. 3. Sharp upper contact between tourmalinized amphibolitic wall rock and schorl-bearing pegmatite, depth of 228 feet, southwest wall of shaft.

FIG. 4. Wall rock inclusions, partially rounded and altered; coarse microline perthite crystal bottom left of center; shaft station, depth 282 feet.

be chilled borders around the inclusions. Crystals in the rims are oriented perpendicular to the edges of the inclusions. Drill intersections strongly indicate that the pegmatite splits and passes above and below two large horses of wall rock at the up-dip edge of the sill (Fig. 5b).

INTERNAL STRUCTURE

The pegmatite has a complex internal structure with striking mineral zoning, and several contrasting mineral assemblages are present. Since some of these are known only from drill cores, and others only from limited exposures in a single shaft, their relationships with one another and their sequence of occurrence from the walls inward are as yet imperfectly understood. It seems best, therefore, to describe first the various assemblages as they appear in drill core or in the shaft exposures and to follow the descriptive material with a discussion of their possible interrelationships, sequence and position in the pegmatite.

Mineral Assemblages

Perthite-plagioclase-quartz-muscovite Assemblage.—This is the outermost assemblage in the pegmatite and is present along both the roof and floor of the sill in contact with the tourmalinized wall rocks (Figs. 3; 5a, b, c). Its composition appears to be uniform throughout the pegmatite. It ranges from 1 to 50 feet in thickness and is commonly thickest along the floor of the sill, especially in the deeper parts and in downward bulges (Fig. 5b). The assemblage occurs in all drill holes except those that collared in the pegmatite in the bed of Bernic Lake. Here this assemblage apparently has been eroded. The texture of the unit is coarse-grained, and it becomes increasingly coarse inward. Crystals of perthite and microcline-perthite up to 4 feet long (parallel to C axis) are contained in a finer-grained matrix of plagioclase (Ab_{95} An_5), quartz and minor muscovite. Although examination of many more specimens and thin sections is required for documentation, it now appears that perthite crystals close to the contact lack microcline twinning and are monoclinic or nearly so, whereas those remote from the contacts are twinned, triclinic microcline-perthite. All the feldspars are definitely pink close to the wall rock contact but this color fades with increasing distance from the contact, the feldspars changing to flesh-colored, gray or white. This effect is probably due to assimilation of some iron from the amphibolitic wall rocks.

Accessory minerals present in this assemblage are black tourmaline, which is characteristic and abundant especially near the wall rock contacts, fine apatite and topaz that have been noted only in thin sections cut close to the contact, and beryl, which occurs as white subhedral crystals that are commonly grouped together in clusters. In the southwest wall of the shaft at the wall rock-pegmatite contact, a wedge-shaped beryl crystal appears to have grown inward, enlarging as it grew, from a point source on the contact. Occasional crystals of columbite have been noted.

Beryl is the only potentially economic mineral in the assemblage and is not known to occur elsewhere in the pegmatite. In view of the small size,

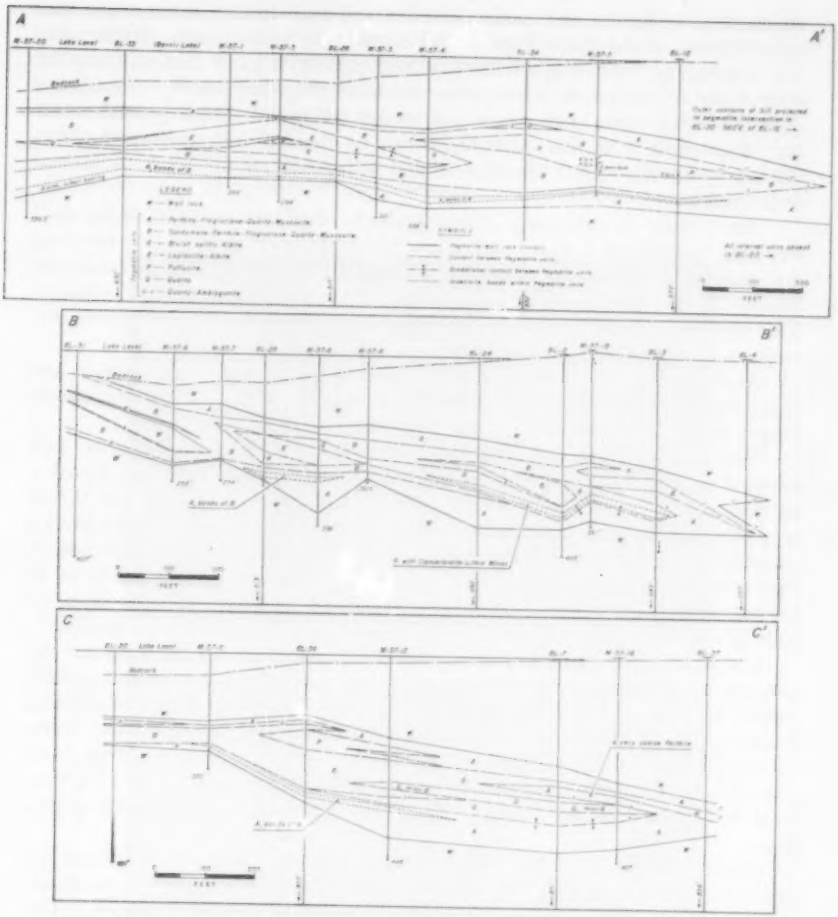

FIG. 5 (a). Section A-A′ strike section or longitudinal section through pollucite and lepidolite units. FIG. 5 (b). Section B-B′ dip section through lepidolite unit. FIG. 5 (c). Section C-C′ dip section through pollucite unit.

irregular distribution and general rarity of beryl in this assemblage, it is unlikely that it could be profitably recovered.

Spodumene-microcline perthite-plagioclase-quartz-muscovite Assemblage.—This assemblage constitutes the chief lithium-bearing unit in the pegmatite. It forms two main layers within the sill, one near the roof that is generally thicker and has a higher concentration of spodumene, and a second close to the floor (Fig. 5). It ranges up to 50 feet in thickness and has a rather wide range in mineral composition depending on the relative amounts of

spodumene, feldspars, and quartz that are present. In drill cores the spodumene content of the assemblage ranges from about 10 to nearly 100 percent.[1] The spodumene assemblage is thickest and highest in Li_2O content along the roof of the sill where, in some places, the assemblage apparently is composed mainly of spodumene with minor quartz and feldspars. Underground workings may show that this assemblage can be divided into two spodumene-bearing units but such a division is not warranted on the basis of present drill results.

The texture is extremely coarse-grained. Spodumene crystals up to 3 feet long (parallel to C axis) and microcline-perthite crystals up to 8 feet long are present. Spodumene, plagioclase (Ab_{95} An_5), quartz and muscovite appear to fill the interstices between the large crystals of potash feldspar. This matrix material is in many places banded, consisting of alternate spodumene-rich and plagioclase-rich layers.

Spodumene is the principal lithium-bearing mineral in the pegmatite and is apparently restricted to this assemblage. Lithia content of this assemblage ranges with the spodumene content from 0.5 to 7.0 percent.

Cleavelandite-lithia mica-quartz Assemblage.—This assemblage is well exposed in the shaft and shaft station at a depth of 282 feet. It forms a narrow rim, 6 inches to two feet wide, around the margins of the bodies of quartz-amblygonite pegmatite described below (Figs. 6 and 7). It contains about 60 percent of cleavelandite (Ab_{95} An_5), 30 percent of zinnwaldite and/or lepidolite, with minor quartz and very minor muscovite. Intersections in several drill holes suggest that this assemblage may also form a layer or zone below the quartz core in the deeper parts of the pegmatite (Fig. 5b).

The texture is medium-grained and the assemblage is characterized by clusters of radiating, platy, white to bluish cleavelandite crystals, saucer-shaped booklets of lavendar zinnwaldite and somewhat finer flakes of purplish lepidolite. The lithia micas also form clusters with radiating crystal habit. In many places the unit is distinctively banded; thin layers of relatively pure cleavelandite alternate with layers rich in lithia micas and quartz (Fig. 6). This banding is parallel to the contact with the quartz-amblygonite assemblage.

Quartz-amblygonite Assemblage.—This unit is composed of about 70 percent massive, grayish quartz and 30 percent amblygonite that forms cream-to-white crystals up to 3 feet in length parallel to C axis (Fig. 7). The assemblage occurs toward the middle of the pegmatite where it ranges up to 15 feet in vertical thickness as indicated by drill hole intersections. It does not, however, appear to form a continuous horizontal layer within the sill.

The assemblage is well exposed in the southeast wall of the shaft and station from a depth of 268 to 282 feet. Here it forms an extremely irregular lens or pod at least 14 feet in vertical extent, up to 8 feet wide and of unknown lateral extent. The lens lies within the spodumene-bearing assemblage but is rimmed by the cleavelandite-lithia mica assemblage (Fig. 7).

In the shaft-station exposure, the assemblage contains a single coarse,

[1] Several 5-foot intersections of virtually pure spodumene were encountered but these probably represent intersections of very large spodumene crystals.

pink topaz crystal, and coarse topaz crystals also occur associated with quartz and amblygonite in one drill intersection. Another drill hole indicates that petalite may also be an accessory mineral component.

Bluish Aplitic Albite Assemblage.—This assemblage forms a layer up to 40 feet thick slightly below the middle of the sill, especially beneath the lepidolite and quartz cores (Fig. 5). So consistent is this occurrence in the drill intersections that it is regarded as a distinctive marker horizon at this point within the sill. It appears to be of widespread lateral extent particularly in the deeper parts of the sill.

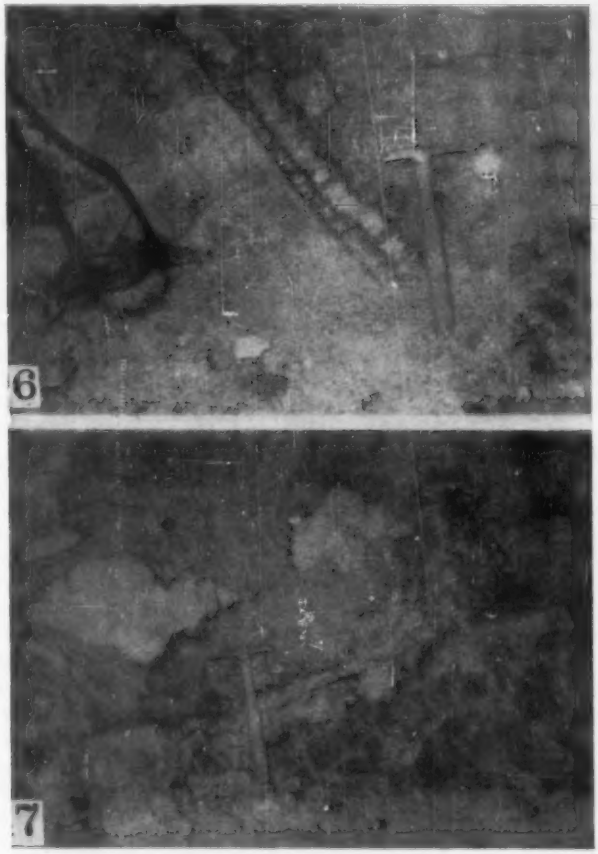

FIG. 6. Quartz-amblygonite assemblage upper right; rimmed by narrow, banded cleavelandite-lithia mica assemblage center; spodumene assemblage lower left; shaft station.

FIG. 7. Coarse white amblygonite crystals in gray quartz; rimmed by cleavelandite (top) and cleavelandite-lithia mica right and bottom center; shaft station.

It is composed almost entirely of albite (Ab_{95} An_5) crystals in an extremely fine-grained aplitic intergrowth that has a distinctive bluish tinge. In thin section the albite is seen to be virtually pure but some patches of quartz and minor muscovite are present. A layer rich in cleavelandite and lithia micas is present within the aplitic albite below the quartz core in the deeper part of the sill (Fig. 5b). No economic minerals have been encountered in this assemblage, which yields uniformly low lithia values.

Pollucite Assemblage.—This assemblage is known only from intersections in five drill holes, where it ranges from 4 to 39 feet in thickness. The drill holes suggest that it forms a continuous horizontal lens extending between these holes near the middle of the sill (Fig. 5a, c). This lens lies in the central and up-dip portion of the sill (Fig. 2) and is elongated in the direction of strike with a bulge perpendicular to this elongation extending down-dip.

The assemblage is composed of almost pure pollucite although in thin section tiny veinlets and stringers containing fine spodumene and a mica, probably lepidolite, transect the pollucite. Thin sections also show the pollucite to contain many tiny inclusions and blebs of quartz. The pollucite forms a dense massive aggregate of fine-grained interlocking crystals. In hand specimens this fine-grained aggregate is composed mainly of white, feldspathic-appearing grains with less abundant colorless, glassy, quartzose-appearing grains but both varieties are pollucite. The mixture of these two types of grains gives the pollucite the appearance of a fine intergrowth consisting of blebs of quartz in a white felsic-appearing matrix. This is a characteristic of the material and is apparently similar to pollucite in the Tin Mountain Pegmatite described by Connolly and O'Hara (2, p. 261). The relationship and difference between the two types of grains is not known. Drill core analyses of megascopically pure material indicate a content of about 28.0% Cs_2O, 1.0% Rb_2O and 0.5% Li_2O. The lithia content is probably due to the spodumene and lepidolite stringers. This material has a hardness of about 6.5 (Moh's scale), a specific gravity of 2.89 and a refractive index of 1.5185.

Lepidolite-albite Assemblage.—This assemblage is known only from intersections in seven drill holes where it ranges from 5 to 36 feet in thickness. Its lateral extent within the pegmatite sill is remarkably similar to that of the pollucite assemblage. Like the latter it apparently forms a horizontal lens continuous between the several drill holes at about the same horizon near the middle of the sill (Fig. 5a, b). It is also located in the central, up-dip portion of the body, is elongated in the direction of strike and has a bulge perpendicular to this elongation extending down-dip (Fig. 2).

The assemblage is composed chiefly of lepidolite but albite (Ab_{95} An_5) is commonly present, ranging from zero to about 40 percent in amount. The lepidolite when pure is purplish and forms a fine-grained, dense, massive intergrowth of randomly oriented, matted flakes. The aggregate is tough and hard, and the fine lepidolite does not flake off readily. Albite when present is fine-grained, white or cream-colored and is intimately intergrown with lepidolite.

The lithia content of this assemblage ranges from 1.0 to 2.5 percent, apparently depending on the amount of albite present and on variations in

lithia content of the mica. Microscope work shows that two micas of slightly differing index are present; the indeces probably reflect different lithia contents.

Quartz Assemblage.—The pegmatite contains an extensive core of massive, colorless, white or gray quartz that forms a thick horizontal lens near the middle of the sill in the down-dip portions (Figs. 2; 5b, c). This quartz lens ranges in thickness from 9 to 79 feet. No accessory minerals have been noted but the assemblage is known only from drill intersections and accessories may be present elsewhere in the body. A similar but thinner horizontal lens of quartz is present in the up-dip part of the sill (Fig. 5a). Also in the upper portions of the pegmatite numerous short intersections (3 to 8 feet) of pure quartz were cut. These do not seem to correlate laterally from hole to hole and are believed to represent irregular, isolated small pods or cores of quartz.

Relationships Between Assemblages

The outermost recognizable unit associated with the pegmatite is the narrow tourmalinized zone that apparently rims the sill. In the Montgary pegmatite it is undoubtedly the result of interaction between wall rock and intruded pegmatite fluid, and is largely composed of altered wall rock material. Pegmatitic additions are minor in amount and are composed mainly of volatile materials.

Thin sections cut across the contact show that there is in places a thin outer selvedge less than ¼ inch wide composed of quartz-muscovite that forms a border zone (1, p. 24). This unit was not recognized in core logging due to its extreme narrowness and because it grades rapidly into the perthite-plagioclase-quartz-muscovite assemblage with which it has been mapped.

The perthite-plagioclase-quartz-muscovite assemblage lies within the border zone both along the roof and floor of the sill and everywhere forms the wall zone (1, p. 32). Both in drill cores and in the shaft (Fig. 3) its contacts with the tourmalinized wall rocks are very sharp. It is generally much thicker along the floor of the sill than at the roof (Fig. 5), and toward the edges of the sill it thickens, both at roof and floor, to form the bulk of the pegmatite. This is due to lateral pinchout of the interior assemblages (Fig. 5c).

The spodumene-bearing assemblage forms the first (outer) intermediate zone in the pegmatite (1, p. 42). In the shaft its contact with the wall zone assemblage is gradational and the change is marked by the appearance and rapid increase in abundance of spodumene inward in the matrix material that surrounds the coarse microcline-perthite crystals. The contact zone is only a few feet thick. Drill intersections show that this contact is also gradational in the lower part of the sill, and here the thick wall zone layer contains several ill-defined bands that are spodumene-bearing (Fig. 5a). This may be apparent banding due to inter-fingering of the two assemblages at the location of the drill intersection. This banding occurs at the floor of the sill but especially in the up-dip extremity of the sill for the spodumene-bearing bands disappear down-dip (Fig. 5b, c). In some places there seems almost to be a telescoping (1, p. 19) of the two units.

In one drill hole the spodumene assemblage fills a tiny fracture to form a sharp-walled veinlet that cuts the wall zone assemblage. It seems definite that the spodumene material originally was fluid and capable of occupying fractures in the already solidified wall zone.

The spodumene unit forms two main layers, one below the roof and the other above the floor of the sill. These branch, redivide and coalesce so that several layers are present in places, but in general the spodumene assemblage encloses most of the remaining assemblages (Fig. 5). Toward the middle of the sill it lies in contact with the cleavelandite-lithia mica, bluish aplitic albite, pollucite and lepidolite assemblages. Only the contact between the spodumene assemblage and the cleavelandite-lithia mica unit is exposed in the shaft station, where it is very sharp and is marked by a sudden change in mineralogy from that of the former to that of the latter (Fig. 6). The other contacts are known only from drill cores, which indicate that the contacts of the spodumene assemblage with both the pollucite and lepidolite assemblages are sharp. Its contacts with the aplitic albite unit, however, are in many places gradational. Fine bluish albite becomes increasingly abundant in the matrix material at the expense of the coarse microcline and spodumene crystals.

The cleavelandite-lithia mica assemblage is known only from the shaft exposures but may have passed unrecognized in core logging due to its very limited thickness. Its relationships are simple for it forms a narrow intermediate zone that lies between the spodumene and quartz-amblygonite assemblages, rimming the latter and in sharp contact with both (Figs. 6, 7).

The bluish aplitic albite assemblage forms a thick inner unit that lies, in general, near the middle of the sill, between the main upper and lower layers of the spodumene assemblage, and particularly beneath the lenticular lepidolite and quartz assemblages (Fig. 5b, c). Its contacts with the lepidolite assemblage are gradational, especially where it underlies the lepidolite (Fig. 5b). Here a very gradual upward increase in lepidolite content occurs with a corresponding decrease in albite; the two units merge gradually into one another. Similar gradational contacts are present where the albite assemblage wraps around and encloses the down-dip edge of the lepidolite lens (Fig. 5a, b). Contacts between the aplitic albite unit and the quartz core in the deeper parts of the sill are sharp (Fig. 5c). Beneath the quartz core the aplitic-albite layer contains an ill-defined band rich in cleavelandite and lithia micas (Fig. 5c) and gradually merges downward into the wall zone assemblage.

The pollucite and lepidolite assemblages probably form conformable internal lenses within the flat sill. In four of five drill holes the pollucite unit is both over-and underlain by the spodumene assemblage. In the fifth hole it is again underlain by this same assemblage but is overlain by the outermost wall zone assemblage (Fig. 5c). Contacts between the pollucite and these enclosing assemblages are all sharp.

In one drill hole (M-57-5, Fig. 5a) a 39-foot pollucite intersection contains two short sections of quartz-amblygonite and one short section of pure spodumene, probably a single large crystal. Contacts between these units

in the core are sharp. It is difficult to interpret relationships from this one intersection but it seems probable that the short quartz-amblygonite sections represent the edges of an irregular pod of this material, here enclosed by pollucite. Underground exposures at this location should prove both interesting and informative in regard to age, physical, and genetic relationships between these units.

In five of seven drill holes the lepidolite unit is overlain by the spodumene assemblage and the contacts are sharp. In the remaining two holes the lepidolite is overlain by the bluish aplitic-albite unit and contacts are gradational. In three holes it is underlain by the same unit with gradational contacts already described (Fig. 5a, b). In two holes lepidolite is underlain by a thin quartz core and in two others by the spodumene assemblage (Fig. 5a, b). Its contacts with these units are sharp.

Lenticular or pod-like cores are formed by the quartz-amblygonite and quartz assemblages. Only the former of these is exposed in the shaft station. Here the quartz-amblygonite unit is an extremely irregular, pod-like core that is not conformable with the flat attitude of the sill. It has sharp contacts with the cleavelandite-lithia mica assemblage which rims it (Figs. 6, 7). Drill intersections suggest that similar pods of quartz-amblygonite probably unconnected, are scattered throughout the pegmatite.

The quartz assemblage forms a thick, lenticular core that is, in general, conformable within the sill in the deeper portions of the pegmatite (Figs. 2; 5b, c). Little is known of its relationships in the pegmatite for it is not exposed, but it was intersected in fourteen drill holes. In all of these it is underlain by the bluish aplitic-albite assemblage and the contacts are sharp. It is overlain in ten holes by the spodumene-bearing assemblage and in four by the wall zone, apparently due to pinchout of the former, and again contacts are sharp. Isolated, small lenticular or pod-like quartz cores are thought to be scattered in the up-dip parts of the sill and these also have sharp contacts with the enclosing assemblages.

DISCUSSION

Introduction.—It is recognized that much of the following discussion involves arguments and concepts that are of controversial nature. It is therefore stressed that the discussion represents the writer's present thoughts based, certainly, on an incomplete knowledge of the deposit. The arguments must be held open to critical evaluation in the light of increasing evidence from both this deposit and from other pegmatites.

Origin.—Numerous features of the deposit indicate that the pegmatite was emplaced as a fluid and that crystallization and differentiation took place in a restricted system. The excellent development of internal structure with pronounced mineral zoning is in accord with this concept for it has been noted (5, p. 14) that pegmatites of replacement origin tend to be homogeneous, whereas those originating through fluid crystallization tend to be zoned. Furthermore the mineral assemblages present, and their sequence of occur-

rence from walls inward are, in general, similar to those described from many other pegmatites and pegmatite districts. This feature strongly supports origin by fluid crystallization, since metasomatism or replacement would hardly be expected to produce such repeatedly consistent relationships.

The nature of the wall rock contacts also lends support to the theory of fluid origin. Extremely sharp contacts are a common characteristic of intrusive relationships, especially when they involve rocks of such different composition as pegmatite and amphibolite. The nature of the wall rock alteration also is in accord with this genetic concept. The alteration is of very limited extent, which would not presumably be the case should the pegmatite have been formed by large scale-metasomatism or replacement of the wall rocks. In addition, the wall rocks within a foot of the contact are fresh, unaltered amphibolites, which again would not be expected if extensive metasomatism had occurred. The nature of the alteration, tourmalinization, and biotization of hornblende is similarly in accord with fluid emplacement and crystallization, since fluorine, boron, and water are believed to be three of the common mineralizers concentrated in pegmatitic differentiates. These would naturally combine at the chamber walls with other constituents, and noteably with iron mobilized from the wall rocks by the heat of intrusion. The sharp, angular contacts of the wall rock inclusions (Fig. 4) also suggest fluid emplacement, although they appear to have been partially rounded and altered by replacement at their margins after they dropped into the fluid-filled chamber. Two drill intersections at the up-dip edge of the sill show that pegmatite surrounds a large septum and a thin wedge-shaped horse of wall rock (Fig. 3b) and the relationships here strongly suggest fluid emplacement.

Certain features of crystal growth in the pegmatite also support the same genetic hypothesis. The general increase in grain and crystal size from the walls inward is to be expected in the case of fluid emplacement due to more rapid cooling at the walls and to progressing crystallization with decreasing viscosities and increasing rates of diffusion. The beryl crystal described above appears to have grown inward from a source on the contact, expanding as it grew. The orientation of this crystal and also of the plagioclase crystals that rim the wall rock inclusions is definitely preferred in a direction perpendicular to the contact. They appear to have been free to grow inward away from the contacts into a fluid phase.

Veining of the outer wall zone assemblage by the inner spodumene-bearing unit as previously described, and the sharp contacts of this veinlet, strongly suggest that this is a tiny fluid-filled fracture. The spodumene assemblage must therefore have been fluid after solidification and fracturing of the wall zone.

The change from untwinned perthite (monoclinic) at the contact to twinned microcline-perthite (triclinic) inward probably results from a lower degree of Si/Al ordering in the former. This condition would be a probable result of higher temperatures and/or more rapid cooling close to the contacts. Again this is in accord with origin by fluid crystallization from the walls inward. There is no recognizable variation in plagioclase composition within the pegmatite. All plagioclase, regardless of its texture or position

in the sill, was found to be of remarkably uniform composition in the middle albite range.

Although none of the above features alone is sufficiently distinctive to prove origin by fluid emplacement and crystallization, yet when considered collectively they present extremely strong evidence in support of such origin. Certainly it is difficult to envisage an alternative theory that would explain all these features.

Relationships Between Attitude and Internal Structure.—It is not the writer's intention to suggest that flat attitude is the only, or indeed the most important causative factor in the development of complex internal structure. The numerous exceptions of steeply dipping, well-zoned pegmatites at once rule out such a broad generalization. It is suggested, however, that attitude is one important factor as is also the degree of restriction of the crystallizing system (4, p. 36). There are doubtless numerous other factors including perhaps initial composition, depth, temperature, and pressure of intrusion, and shape and size.

If, however, zoned or differentiated pegmatites originate by crystallization of an intruded fluid in a restricted system, then the attitude of the crystallizing body should exert some influence on the formation and distribution of the various units of internal structure within the pegmatite. In the case of two tabular, fluid-filled chambers of the same dimensions, one of which is horizontal and the other vertical, then in the former, any tendency for crystal settling or gravitational differentiation should be facilitated in comparison to the latter. This should lead to more pronounced development of internal structure in the flat body. In both the southeastern Manitoba (3, 9, 10) and Alto Ligonha, Portuguese East Africa (6) pegmatite districts, flat-lying bodies exhibit more complex and better developed internal structure than steep bodies.[2]

Furthermore as gravitational differentiation and crystal settling proceed within a flat-lying, fluid-filled chamber, the early-formed heavier constituents should be concentrated at the floor. Volatile materials would tend to concentrate at the roof. Thus the earliest-formed assemblage should be thicker and finer grained along the floor than along the roof, and should reach maximum thickness where it fills depressions in the floor. Certainly this is the case in the Montgary pegmatite (Fig. 5). Similarly the same processes should result in gradational contacts between assemblages in the lower parts of the sill since, when crystallization of a new mineral commenced, crystal settling of earlier-formed constituents from a higher point within the sill could cause co-deposition of earlier and later formed minerals on the chamber floor. Conversely this effect should be minimized along the roof where crystal or gravitational settling would rapidly cause downward removal of earlier-formed crystals. Later minerals and their assemblages should thus be unpolluted by early constituents, and contacts between units should be sharp along the roof of the sill. Again, these are the observed relationships in the Montgary deposit (Fig. 5).

Thus it seems that horizontal attitude should facilitate development of

[2] This is true also of numerous basic and ultrabasic sills of igneous origin.

internal structure. The contrasts in internal structure between the upper and lower portions of the Montgary pegmatite are in accordance with this concept and therefore also appear to support the fluid crystallization theory of origin. They also suggest that the Montgary deposit occupied a flat chamber at the time of its formation, and this attitude has not changed appreciably since that time.

Origin of the Pollucite, Lepidolite and Albite Assemblages.—The remarkable similarities between the pollucite and lepidolite assemblages have already been noted and these represent one of the most interesting aspects of the deposit.

The two assemblages are almost identical in size; their horizontal dimensions as outlined in Figure 2 are virtually the same, as are their thicknesses and total contained tonnages. Their close similarity in shape can also be seen in Figure 2 where, indeed, they display remarkable bilateral symmetry. Both are elongated in the same trend parallel to the strike of the sill, and both have a pronounced bulge normal to this elongation that extends down-dip. Their disposition within the pegmatite is identical; both assemblages form conformable internal core-like lenses near the centre of the up-dip edge of the sill.

In regard to texture both units are fine-grained in contrast with the coarse pegmatitic nature of most of the other units, and both pollucite and lepidolite occur in dense, massive intergrowths of granular, anhedral crystals. In mineralogic composition both are similar in being essentially monomineralic [3] and quartz-deficient, again contrasting with all the other units of the pegmatite. In chemical composition it is noteworthy that both pollucite and lepidolite are hydrous aluminum silicates of rare alkalis.

The extensive list of similarities between the pollucite and lepidolite assemblages can hardly be coincidental. They suggest that the two units are closely related as to genesis and time of formation within the pegmatite and perhaps distinct, somehow, from the other assemblages of the deposit. If the two units are internal segregated cores formed late in the process of crystallization and differentiation in a restricted system, it is difficult, indeed, to visualize the unique conditions that must have pertained within the pegmatite leading to the virtually complete segregation of lithium from caesium. Moreover internal pod-like zones or cores of polyzonal pegmatites are noteably irregular (1, p. 55) as in the case of the quartz-amblygonite assemblage in this deposit; hence the remarkable similarity of shape and occurrence of the pollucite and lepidolite units is not in accord with the observed characteristics of such cores. It is suggested that these two units are of later replacement origin resulting from a later stage in pegmatite formation. Such late replacement units are commonly conformable, in general, with earlier-formed zones (1, p. 86, Fig. 65B) and with external structure.

Unfortunately underground exposures of the units that should assist in solving the problem do not exist at present. The lepidolite assemblage, however, does appear in section (Fig. 5a) to cut across other units of internal

[3] Except where lepidolite grades through a zone of increasing albite into the bluish aplitic albite assemblage. The latter is discussed below.

structure which is suggestive of replacement. There is, moreover, abundant literature clearly indicating that pollucite, and to a lesser degree lepidolite, are both late replacements of earlier-formed constituents, and late fracture-filling minerals in other pegmatites. Dymkov (4) describes and presents drawings of photomicrographs of pollucite from East Khazakstan pegmatites that is pseudomorphic after tourmaline, spodumene, petalite, and that fills cavities or veinlets. It is noteworthy that pollucite in these drawings is almost always accompanied by a fine, scaley lepidolite, a description that could well be applied to the lepidolite unit in the Montgary deposit. Schwartz (8, p. 282) likewise describes a probable pollucite pseudomorph after amblygonite from the Tin Mountain Pegmatite in South Dakota. Quensel (7, p. 119, Plate II) describes both pollucite and lepidolite in the Varuträsk Pegmatite as replacement units, and assigns both to the higher temperature phase of his pneumatogenic stage of pegmatite formation. Thus it is clear that pollucite is commonly a late-formed consituent in complex pegmatites that replaces earlier minerals. Furthermore it is generally associated with fine scaley lepidolite, and this lends support to the theory that these assemblages in the Montgary pegmatite have a similar origin.

Many of the characteristics of the pollucite and lepidolite previously mentioned also apply to the bluish aplitic-albite assemblage that is closely related to lepidolite spatially within the sill (Fig. 5a, b). Like both lepidolite and pollucite the albite unit is extremely fine-grained and forms a dense, massive intergrowth. It also is monomineralic, quartz-deficient, and is composed of the aluminum silicate of sodium, again an alkali. It is probable that this albite assemblage is also of late replacement origin and its gradational and ill-defined contacts with lepidolite and with the wall zone assemblage (Fig. 5c) are in accord with such origin. Quensel (7, p. 119, Plate II) has proposed the same origin for saccharoidal albite in the Varuträsk pegmatite and has assigned it to the lower temperature phase of his pneumatogenic stage. The saccharoidal description is certainly applicable to the bluish aplitic-albite of the Montgary deposit which, indeed, appears to be remarkably similar to the Varuträsk body.

The question of origin of the late caesium, lithium, and sodium replacement solutions is a difficult problem. Since it seems certain that the complex pegmatites result from fluid crystallization in a restricted system, the solutions must originate within the crystallizing pegmatite itself, and must result from processes operating therein. It is known that cooling of early-formed potash feldspars causes unmixing of soda, yielding perthite, and that in some cases albite is formed from the unmixed component beyond the boundaries of the parent potash feldspar crystal (5, p. 37). This suggests a possible mechanism for the origin of the late solutions. Perhaps caesium and lithium are also taken up in early-formed feldspars [4] when ionic size requirements are not restrictive due to high temperature, only to be released by unmixing when cooling later places prohibitive limits on ionic size. It is also possible that the late solutions originate simply in the last stage of crystallization, with con-

[4] Lithium may also substitute for aluminum in mica structures.

centration of the rarer alkalies and other elements together with water. Discharge of this material into any available avenue of escape could result in late replacement and fracture filling and could result in solid lenses if replacement were carried to completion at a particular locality. Perhaps both processes are operative and contribute to the late solutions.

SUMMARY

In summary it is proposed that the Montgary pegmatite was emplaced as a fluid in a flat fracture that cut amphibolitic host rocks. Alteration of these rocks was minor, chiefly tourmalinization along the contacts. Crystallization of the fluid took place in a restricted system within this flat chamber and led to the development of several mineral assemblages that form zones or cores. From walls inward these include the perthite-plagioclase-quartz-muscovite assemblage, the spodumene-microcline perthite-plagioclase-quartz-muscovite assemblage, the cleavelandite-lithia micas-quartz assemblage and cores of quartz-amblygonite and quartz. These units are thought to represent Quensel's pegmatitic stage of pegmatite formation. Subsequently a late generation of solutions occurred, perhaps as a consequence of normal crystallization and differentiation, or perhaps by unmixing of alkalis from earlier-formed silicates. The late solutions formed the pollucite, lepidolite, and albite assemblages in the interior of the sill, probably by replacement of the earlier pegmatitic stage units. The late solutions and their assemblages are believed to represent Quensel's pneumatogenic stage of pegmatite formation.

TORONTO, ONTARIO,
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TRACE LEAD IN POTASH FELDSPARS ASSOCIATED WITH ORE DEPOSITS

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ABSTRACT

The amount of trace lead in potash feldspars can be correlated with the lead ore deposits associated with igneous rocks. The lead content of potassium feldspars separated from several quartz monzonite intrusives of the Basin and Range province has been determined spectrochemically. Samples were collected from the Tintic, West Mountain (Bingham), Park City-Little Cottonwood, and Iron Springs mining districts in Utah, and from the Robinson mining district and the Whitehorse Pass area in Nevada.

A spectrochemical precision of $\pm 12\%$ was obtained using an internal standard of bismuth. The accuracy of selected analyses were checked independently.

Each mining district or area sampled belongs to a different trace lead population. The mean lead concentrations and the standard deviations are:

1. Robinson mining district, 14 ± 6 ppm lead,
2. Iron Springs mining district, 15 ± 3 ppm lead,
3. Tintic mining district, 29 ± 10 ppm lead,
4. Whitehorse Pass area, 41 ± 8 ppm lead,
5. Park City-Little Cottonwood mining district, 47 ± 20 ppm lead,
6. West Mountain (Bingham) mining district, 61 ± 30 ppm lead.

The potassium feldspars from lead mining districts have a higher trace lead content than those from areas where there is no lead production, or where lead production is not significant.

The potassium feldspars from hydrothermally altered intrusives contain less lead than spatially related unaltered intrusives.

INTRODUCTION

SPECULATION as to whether the trace lead in potash feldspars can be correlated with the lead ore deposits associated with igneous rocks has followed two lines of thought. Direct reasoning would assume that a high trace lead concentration in the original magma would result in a high trace lead concentration in potash feldspars and would leave a residuum lead content sufficient to form ore deposits. However, Ingerson (6) has speculated as to whether lead mineral deposits might be formed when the physico-chemical conditions within a cooling intrusive were such as to prevent the lead ions from entering the silicate structure of the feldspars. Thus the lead ions that are not fixed in the essential magmatic minerals seem destined to form ore deposits. This process would result in low trace lead concentrations in the magmatic minerals associated with ore deposits, whereas, high trace content would be indicative of non-economic deposits. This first trace lead study of igneous rocks in Utah and Nevada supports the first hypothesis and indicates that there is a direct correlation between the trace lead in magmatic feldspars and the concentration of lead minerals in associated ore deposits.

Goldschmidt (5) has set forth the crystal-chemical conditions that must be satisfied for divalent lead (Pb^{+2}) to substitute for the potassium ion (K^{+1}) in the feldspar structure. The ionic radii of Pb^{+2} (1.32Å) and K^{+1} (1.33Å) are nearly equal. In order to equalize the electrovalent charge for each Pb^{+2} capture an Al^{+3} ion must be admitted in place of a Si^{+4} ion as in the following equation:

$$KAlSi_3O_8 + Pb^{+2} + Al^{+3} = PbAl_2Si_2O_8 + K^{+1} + Si^{+4}$$

If the growth of a potash feldspar crystal may be visualized as the accretion of $KAlSi_3O_8$ units, statistically there will be occasions when the ionic grouping of $PbAl_2Si_2O_8$ will occur. This is a thermodynamically stable structure (11) which has the geometry of orthoclase (7).

How much lead will be fixed in this structure depends upon chemical composition, temperature, pressure, and electric, magnetic and gravity fields. This study indicates the concentration of lead in the original magma is the dominant factor in determining the trace lead content of the potassium feldspars in the igneous rocks investigated.

The rocks studied are all from quartz monzonite stocks of the Basin and Range province. The age of each of these intrusive stocks is about the same. Eardley (4) states the consensus of opinion is to place the time of the intrusions in the late Eocene.[2] These intrusives are younger than the most intense portion of the Laramide, as the intrusions cut Laramide structures.

[2] Isotopic age determinations have substantiated this opinion. The intrusive age of the Silver City stock was determined to be middle Eocene (9). The Alta stock has been given a late Eocene age (3).

FIG. 1. Index map showing the areas sampled.

These stocks have not been dynamothermally metamorphosed by later orogenies.

Figure 1 is an index map indicating the location of the districts and areas investigated.

Unweathered specimens were collected from outcrops wherever possible. A few float or talus samples were obtained and are so indicated in the tables.

PROCEDURES

Sample Preparation.—The samples were crushed and a portion of the product was pulverized in a disc-type pulverizer. The pulverizer was fitted with mullite ($3Al_2O_3 \cdot 2SiO_2$) grinding plates to prevent metal contamination.

The magnetite, in quantities ranging from a trace to greater than 10 percent, was easily removed from the washed and dried samples with a small Alnico magnet. The ferromagnesium minerals and those light-colored minerals containing magnetic inclusions, were removed with an electromagnetic separator. The residue consisted primarily of quartz, plagioclase and potash feldspars.

The potash feldspars were then separated readily from plagioclase feldspar and quartz on the basis of specific gravity differences with heavy liquids. As the specific gravities were close to one another, the separation process was speeded up by the use of a small centrifuge.

The concentrates were checked with a petrographic microscope and were found to be more than 95 percent potash feldspar.

Sample Analysis.—The potash feldspars were analyzed spectrochemically for lead. The analyses were made with a 1.5 meter, 24,400 line per inch, Abney-mounted grating spectrograph. Precise quantitative results were obtained by adding an internal standard. The direct current anode excitation spectra were recorded on film and the line intensities were measured with a photoelectric densitometer.

Potash feldspars do not contain a suitable internal standard for lead analyses; therefore, Bismuth III oxide (Bi_2O_3) was added to each sample. The 2809.625Å bismuth line was chosen because it lies close to the best lead line (2833.069Å) and its intensity is of the same order of magnitude. The feldspars have no detectable natural bismuth content and the interference of extraneous elements is negligible.

About 15 mg of the standardized feldspar were arced in a purified graphite electrode with a 50 percent mixture of powdered graphite and sodium nitrate.

Each sample was analyzed three times. The arcing time in each case was 80 seconds. This allowed a 40 second analysis arcing; then the camera was racked and a 40 second insurance arcing was made. The second 40 seconds was to insure that all the lead had volatilized.

COLLECTED DATA

The Tintic Mining District, Utah.[3]—The Tintic mining district lies about 60 miles southwest of Salt Lake City, Utah, in the East Tintic Mountains. This mountain range has the general north–south trend of the Basin and Range province. A series of folds in Precambrian to Permian sediments whose axes also have a north–south trend cross the range in the vicinity of Eureka, Utah. Several miles south of Eureka these folds are truncated by the Silver City, Swansea, and Sunrise Peak stocks, all of monzonitic composition. In this investigation only the Silver City stock was sampled (with the exception of Sample 103). The mineralization in this district is fissure filling, fissure replacement and bedding replacement in character. The intrusives themselves are mineralized only in sparse fissures.

Production of recoverable lead from 1916–1953 was 627,600 tons (13).

ANALYTICAL RESULTS

No. of samples	Sample location	Mean ppm Pb*	Range of values ppm Pb
9	Silver City stock	29 ± 10	10 ± 1 to 44 ± 3
1	Swansea stock	27 ± 2	—
Total 10	Tintic district	29 ± 10	10 ± 1 to 44 ± 3

* Mean ppm $= \frac{\Sigma x_i}{n} \pm \left[\frac{\Sigma (\bar{x} - x_i)^2}{n-1}\right]^{\frac{1}{2}}$.

[3] Abstracted from Utah Geol. Soc. (14).

The West Mountain (Bingham) District, Utah.[4]—The West Mountain district situated some 20 miles southwest of Salt Lake City, Utah, is better known as the Bingham copper district, but it has also produced large quantities of lead and zinc. The intrusives of the district consist of two stocks within dipping Pennsylvanian sediments. The block faulting of these sediments form the Oquirrh Mountains, which are typical of the Basin and Range province. The Bingham stock is the location of a large open pit copper deposit and the adjacent Last Chance stock is essentially non-mineralized. Stringham (12) has shown the Bingham rocks to be variable from granite to granodiorite with the more granitic types predominating. The Last Chance stock is very uniformly a quartz monzonite to quartz monzonite porphyry.

The samples collected from the Bingham and Last Chance stocks were from different portions of the stocks and were all quartz monzonites. The mineralization of the Bingham stock is a lowgrade dissemination of copper sulfides; whereas, the lead and zinc are mined from replacement deposits adjacent to the stock.

Production of recoverable lead from 1916–1953 was 1,313,750 tons (13).

ANALYTICAL RESULTS

No. of samples	Sample location	Mean ppm Pb	Range of values ppm Pb
12	Bingham stock	44 ± 20	11 ± 1 to 79 ± 5
10	Last Chance stock	80 ± 27	50 ± 3 to 126 ± 9
Total 22	West Mountain district	61 ± 30	11 ± 1 to 126 ± 9

The Robinson Mining District, Nevada.[5]—The district, extending for about six miles westward from Ely, Nevada, has been described as one of the "porphyry coppers" of the Basin and Range province. A number of individual intrusive stocks line up along an east–west anticline. The anticlinal structure of Paleozoic sediments is by no means continuous as several major north–south faults have broken its back. Toward the western end of the district, the beds are overturned in association with longitudinal faults. The intrusives along the anticlinal axis are believed to belong to two periods of injection. The older intrusions are mineralized to a greater degree than the younger intrusions. The difference is attributed to different degrees of fracturing. The principal metallic minerals are chalcopyrite and pyrite, but minor ore minerals of gold, lead, zinc, silver and manganese are present.

The United States Bureau of Mines (13) has not listed the Robinson district as a lead producer.

Most of the samples were taken from the hydrothermally altered and mineralized areas.

[4] Abstracted from Stringham (12).
[5] Abstracted from Newhouse (10).

ANALYTICAL RESULTS

No. of samples	Sample location	Mean ppm Pb	Range of values ppm Pb
2	Weary Flat stock	20 ± 4	17 ± 0 to 23 ± 2
11	Liberty Pit stock	12 ± 2	10 ± 1 to 16 ± 1
2	Near Keystone Junction	15 ± 1	15 ± 1
1	Kimbley Pit stock	13 ± 1	—
5	Tripp Pit stock	15 ± 6	10 ± 1 to 21 ± 1
4	Veteran Pit stock	12 ± 1	11 ± 1 to 14 ± 1
2	North of Veteran Pit	23 ± 14	9 ± 1 to 37 ± 3
Total 25	Robinson district	14 ± 6	9 ± 1 to 37 ± 3

Park City-Little Cottonwood Districts, Utah.[6]—The Park City and Little Cottonwood districts lie adjacent to one another at the intersection of the Wasatch Range and the westward extension of the Uinta arch. Both of these districts were producing lead, zinc, gold and silver long before the turn of the century. Almost all of the ore is found in the sediments, which are strongly folded and faulted around three intrusive stocks. The stocks from east to west are the Clayton Peak stock, the Alta stock and the Little Cottonwood stock. In the order named, they are known as diorite, granodiorite, and quartz monzonite. The degree of mineralization, both vein and replacement, decreases from east to west, but the intrusive rocks are only scarcely mineralized.

The production of recoverable lead from the mined sulfides amounted to 685,680 tons between 1916–1953 (13).

Hand specimens from the Clayton Peak stock show extreme variability in texture and composition; whereas, the other two stocks are uniform throughout.

ANALYTICAL RESULTS

No. of samples	Sample location	Mean ppm Pb	Range of values ppm Pb
1	Alta stock	44 ± 3	—
6	Little Cottonwood stock	55 ± 18	37 ± 3 to 85 ± 6
14	Clayton Peak stock	44 ± 21	10 ± 1 to 75 ± 5
Total 21	Park City-Little Cottonwood district	47 ± 20	10 ± 1 to 85 ± 6

Iron Springs District, Utah.[7]—The Iron Springs district located in southwestern Utah is one of the West's important iron deposits. The three major quartz monzonite porphyry stocks present have been interpreted as laccoliths. The mineralization is strictly contact in character. Both magnetite and hematite occur in the contact zones.

As far as it can be determined, no lead ore has been shipped from this district (13).

[6] Abstracted from Boutwell (1) and Calkins (2).
[7] Abstracted from Lindgren (8).

ANALYTICAL RESULTS

No. of samples	Sample location	Mean ppm Pb	Range of values ppm Pb
2	Iron Mountain stock	17 ± 1	16 ± 1 to 18 ± 1
1	Granite Mountain stock	12 ± 1	—
Total 3	Iron Springs district	15 ± 3	12 ± 1 to 18 ± 1

Whitehorse Pass Area, Eastern Nevada.[8]—Near Whitehorse Pass, about 40 miles southwest of Wendover, Nevada, lies the Whitehorse stock. This stock as described by Adair (personal communication) is a quartz monzonite in gross composition with both coarse and fine grained facies. The pluton lies at the southern extremity of a broad north–south anticline of Devonian and Mississippian sediments. Known mineralization is insignificant and only observed at the contact of igneous and sedimentary rocks. The samples, including both textural types, from which the potash feldspars were separated were generously donated by Mr. Adair.

ANALYTICAL RESULTS

No. of samples	Sample location	Mean ppm Pb	Range of values ppm Pb
2	Whitehorse Pass stock Quartz monzonite	50 ± 1	50 ± 3 to 51 ± 3
4	Whitehorse Pass stock Quartz monzonite porphyry	36 ± 2	34 ± 2 to 38 ± 3
Total 6	Whitehorse Pass stock	41 ± 8	34 ± 2 to 51 ± 3

DATA ANALYSIS

Precision and Accuracy of the Data.—The precision of the analytical method was ± 12 percent. One sample, Number 304, was analyzed 65 times. This sample was included with each group of five other samples analyzed. Throughout the period of the analyses, only random variations of the lead values of sample Number 304 were recognized. An accurate measure of the precision was calculated. The arithmatic mean of these 65 analyses is

$$\bar{X} = \frac{\sum x_i}{n} = 17 \text{ ppm},$$

where the x_i's are the individual analyses and n is the number of analyses. The standard deviation s and the relative deviation C were calculated as follows:

$$s = \pm \left[\frac{\sum (\bar{x} - x_i)^2}{n - 1} \right]^{\frac{1}{2}} = \pm 2 \text{ ppm};$$

$$C = \frac{s}{x} \cdot 100 = \pm 12\%.$$

[8] D. H. Adair, Graduate Student, University of Utah (personal communication, 1957).

TABLE 1

INTERLAB CORRELATIONS

Sample	Description	Slawson's Pb value in ppm	Hall's Pb value in ppm
109	Granite porphyry (Silver City stock, Tintic district, Utah)	44 ± 3	47
218	Quartz monzonite porphyry (Bingham stock, Bingham, Utah)	57 ± 4	53
227	Quartz monzonite porphyry (Last Chance stock, Bingham, Utah)	109 ± 7	106
303	Quartz monzonite porphyry (Liberty pit, Ely, Nevada)	10 ± 1	11
304	Quartz monzonite porphyry (Weary Flat stock, Ely, Nevada)	17 ± 0	17
391	Quartz monzonite porphyry (North of the Veteran pit, Ely, Nevada)	37 ± 3	22

Several of the separated feldspars were sent to the laboratory of the Texas Company, Bellaire, Texas, where the analyses were checked spectrographically by Mr. W. Hall using iron as an internal standard. The results are compared in Table 1.

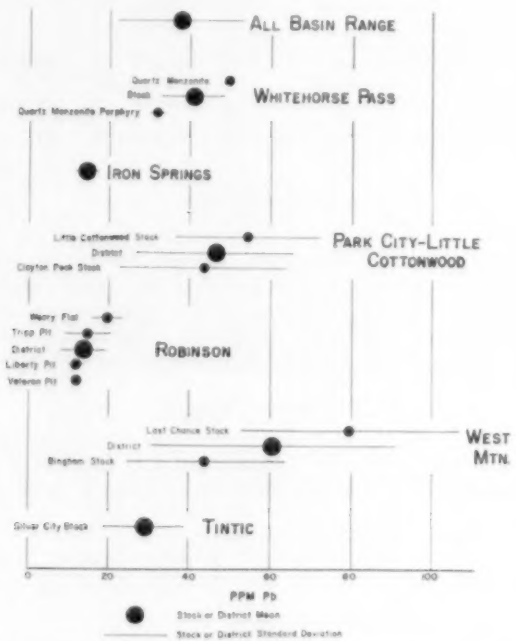

FIG. 2. Comparison of the means and standard deviations of the trace lead in K-feldspars from the sampled areas.

TABLE 2

STATISTICAL COMPARISON OF DATA AT .90 CONFIDENCE LEVEL
(Considering the Right-Tail Area Only)

Areas or Stocks Compared	F-test	Student's t-test
Silver City stock West Mountain district	Significant	——
Silver City stock Robinson district	Significant	——
Silver City stock Park City-Little Cottonwood districts	Significant	——
Silver City stock Iron Springs district	Non-significant	Significant
Silver City stock Whitehorse Pass stock	Non-significant	Significant
West Mountain district Robinson district	Significant	——
West Mountain district Park City-Little Cottonwood districts	Significant	——
West Mountain district Iron Springs district	Non-significant	Significant
West Mountain district Whitehorse Pass stock	Significant	——
Robinson district Park City-Little Cottonwood districts	Significant	——
Robinson district Iron Springs district	Non-significant	Non-significant
Robinson district Whitehorse Pass stock	Non-significant	Significant
Park City-Little Cottonwood districts Iron Springs district	Significant	——
Park City-Little Cottonwood districts Whitehorse Pass stock	Significant	——
Iron Springs district Whitehorse Pass stock	Non-significant	Significant
West Mountain district Bingham stock	Significant	——
West Mountain district Last Chance stock	Non-significant	Significant
Last Chance stock Bingham stock	Non-significant	Significant
Robinson district Liberty pit	Significant	——
Robinson district Tripp pit	Non-significant	Non-significant
Robinson district Veteran pit	Significant	——
Liberty pit Tripp pit	Significant	——
Liberty pit Veteran pit	Non-significant	Non-significant

TABLE 2—*Continued*

Areas or Stocks Compared	F-test	Student's t-test
Tripp pit Veteran pit	Significant	——
Robinson district Weary Flat stock	Non-significant	Significant
Park City-Little Cottonwood districts Cottonwood stock	Non-significant	Non-significant
Park City-Little Cottonwood districts Clayton Peak stock	Non-significant	Non-significant
Clayton Peak stock Cottonwood stock	Non-significant	Non-significant
Quartz Monzonite Quartz Monzonite Porphyry (Whitehorse Pass stock)	Non-significant	Significant

Statistical Treatment of the Data.—The relationship of the lead content of the potash feldspars from the different areas may be seen from Figure 2, which shows the means and standard deviations of the trace leads from the districts and stocks sampled. The means range from 14 ppm to 80 ppm.

Mathematics provides a method to test the equivalence of the mean values of two sample populations and to determine if these samples are members of the same population. This is called the t-test.

The derivation of the t-test is based upon the statistical equivalence of the variances [9] of the two sample populations. The equivalence of the variances may be demonstrated by use of the F-test.

When dealing with a relatively small number of samples, Student's t-test is used for testing the equality of sample means. In applying the F- and Student's t-tests, a null hypothesis is postulated which states that no difference exists between the sample populations. Proof of the hypothesis, a *non-significant* test, at the chosen confidence level is given when the calculated value is less than the value tabulated in any standard statistics text. A calculated value that is larger than the tabulated entry yields a *significant* test which suggests that the compared populations are members of different populations.

The validity of the F-test and Student's t-test that have been used to correlate the concentration populations, require two conditions. The distribution of the means of samples involved must be normal, and the sample population must be representative of the population sampled.

When the distribution of the values within the individual areas are examined, it appears that a normal distribution is approached. The histograms plotted on Figure 3 show this for the Silver City stock, the West Mountain district, the Robinson district and the Park City-Little Cottonwood districts.

It is hoped the samples collected for this investigation are representative of the districts and stocks sampled. This is subject to question and may be resolved only by collecting and analyzing more feldspars.

[9] Variance = (standard deviation)^2.

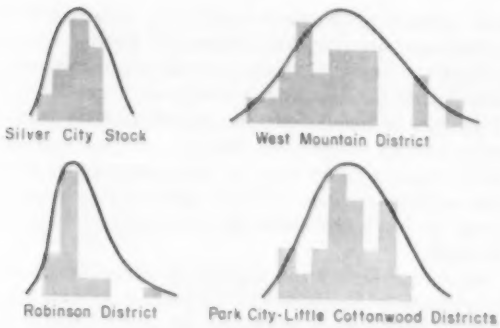

FIG. 3. Trace lead histograms of the four major districts showing approach to normal distribution.

It is felt that in the cases of the stocks shown in Figure 3, that normal distribution is approached and the sampling is representative. Although only the areas cited appear to fulfill the requirements previously stated, the statistical tests also were made in situations involving less than ten samples. Table 2 lists the results of the F- and Student's t-tests which were carried out at a .90 confidence level.

CONCLUSIONS

Several general conclusions can be made concerning the number and distribution of samples necessary in a trace element study of individual igneous rock minerals. In addition, the three following specific conclusions are drawn. A distinct trace lead population characterizes each district sampled. Hydrothermal alteration was found to have an effect on the trace lead content of the potash feldspars. The lead concentration in the potash feldspars may be used in the geochemical exploration for lead.

The optimum number of samples required to represent a stock is not determinable from the data, but it is felt that a minimum of ten samples from each stock is necessary. This conclusion is somewhat arbitrary, as no numerical data are available to substantiate it.

The sample pattern that gives the best representation of a stock has not been determined. In this investigation the samples were taken over as wide an area as practicable. This proved quite satisfactory, as trends are not observed in the lead content of the potash feldspars within a given stock.

The statistical comparisons indicate quite clearly that each area investigated belongs to a separate trace lead population (Table 2). The only comparison in which this is not upheld is between the Robinson and Iron Springs districts. This is probably because the mean and standard deviation for the Iron Springs district are based on only three samples.

Table 2 shows that stocks within a mining district may or may not belong to significantly different lead populations. Two reasons are suggested to explain this behavior. The prime consideration is whether or not the data are representative of the stock. In the West Mountain district, data for

the Last Chance stock and Bingham stock are sufficient to warrant using statistical comparison tests. In the Robinson district, the samples come predominately from one stock (Liberty pit) and therefore, the results of the comparisons between Robinson district stocks may not be valid. Although the number of samples is insufficient, the statistical tests may show relationships that require further research to resolve. As for example, the Whitehorse Pass stock requires more data to determine whether two trace lead populations exist within the stock. On the basis of six analyses there appears to be a difference in the lead content of the potash feldspars related to the grain size of the rock.

A second reason for significant population differences existing within a district can be reasonably attributed to hydrothermal alteration. The comparison tests show the Bingham stock and the Last Chance stock belong to different trace lead populations; whereas, the potash feldspars of the Little Cottonwood and Clayton Peak stocks yield a non-significant result. The Bingham stock is highly altered and contains less lead than the Last Chance stock which is unaltered, while both the Little Cottonwood and Clayton Peak stocks are generally unaltered and contain similar quantities of lead. In the Robinson district, the Weary Flat stock contains more lead than the altered intrusives, but in this case there are only two samples from Weary Flat. The generalization may be made that hydrothermal alteration lowers the trace lead content of the potash feldspars.

There is a correlation between high trace lead concentrations in the potash feldspars and districts known for their lead production. If the mean trace lead values for the various areas are compared to Wedepohl's (15) average lead content of potash feldspars (25 ppm), an interesting observation can be made. The Tintic district as represented by the Silver City stock has a mean value of 29 ppm. The West Mountain (Bingham) district (61 ppm) and the Park City-Little Cottonwood districts (47 ppm) have mean values greater than Wedepohl's (15) mean (25 ppm) for the potash feldspars. These districts have all been major lead producers over the last half century.

Two districts have mean lead concentrations less than 25 ppm. These are the Robinson (14 ppm) and the Iron Springs (15 ppm) districts. Lead production from the Robinson district has been minor and no lead production has been reported from the Iron Springs district. Anomalously, the feldspars from the Whitehorse Pass stock have a high lead content (mean 41 ppm), but the area is not known to be mineralized. As far as it is known, no large-scale exploration programs have been undertaken in this area.

As a result of this investigation, the trace element content of igneous rock minerals may delineate areas that justify further exploration. As far as Basin and Range quartz monzonite stocks are concerned, the trace lead content of potassium feldspars may be used as a guide in reconnaissance-type geochemical exploration for lead.

ACKNOWLEDGMENTS

I wish to express my appreciation to all those who had a hand in furthering this project. Dr. M. P. Nackowski (Mining and Geological Engineering

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MINERALOGY AND TEXTURE OF THE MANGANESE ORE BODIES OF DONGARI BUZURG, BHANDARA DISTRICT, BOMBAY STATE, INDIA, WITH A NOTE ON THEIR GENESIS

SUPRIYA ROY

ABSTRACT

Dongari Buzurg, Bhandara Dt., Bombay State, is an important manganese ore-producing area in India, where the ore bodies are broadly two types: 1) Massive ore bodies associated with the gondites (chiefly spessertite-quartz rock with or without manganese silicates), and 2) Cavernous, botryoidal, kidney shaped, banded, principally manganese dioxide ores as replacement bodies in mica schists and gondites. Mineragraphic studies and X-ray powder analysis, whenever needed, indicated the presence of the following mineral assemblages: 1) Braunite-jacobsite-manganite-vredenburgite-pyrolusite-cryptomelane (+ psilomelane) assemblage for the massive gonditic ores, where cryptomelane and some pyrolusite are secondary oxidation products: 2) psilomelane-cryptomelane-pyrolusite-coronadite-manganite assemblage where the minerals form colloform bands or needles typical of colloidal deposition in open space. Some of pyrolusite is secondary in these ores. In the mixed ore of the above two types, jacobsite and rarely braunite grains are included or engulfed by later pyrolusite or cryptomelane of colloidal origin but no replacement relation is observed.

The paragenetic sequence of the ore minerals has been based on data furnished by the textural relationships. The massive gonditic ores are the earliest to form with the braunite, pyrolusite, manganite and hausmannite-free jacobsite appearing at the initial stage where the ores exhibit a schistose, linear arrangement. At the next stage with the elevation of temperature due to metamorphism, recrystallization occurred resulting in coarse braunite and jacobsite with exsolution of hausmannite lamellae induced in the latter. Primary pyrolusite and manganite vanished at this stage. Well after the formation of these ores of metamorphic derivation, influx of the colloidal gel in the porous and highly foliated mica schist and presumably partially leached gondites, gave rise to the colloform ores principally of the cryptomelane-psilomelane-pyrolusite-coronadite-manganite assemblage. The effect of this invading colloidal gel on metamorphic ores is negligible excepting that the latter is engulfed by the former without any large scale replacement.

The origin of these ores, therefore, is attributed in part to metamorphism of manganiferous sediments, and also to colloidal deposition, contrary to the earlier belief that the manganese dioxide ores of this area are principally the product of supergene alteration of gondites and braunite ore in situ.

INTRODUCTION

Dongari Buzurg, Bhandara Dt., Bombay State, is an important manganese ore-producing area in India. It is situated in a 130 miles long and 16 miles wide belt of manganese ore deposits that cross the two states of Madhya Pradesh and Bombay, and includes a number of important deposits such as

Tirodi, Sitapathor, Sukli, Sitasaongi etc. (Figs. 1, 2). This manganese ore belt of rather unusually large dimensions, has been studied in detail by Fermor (3), who, in his voluminous memoir indicated that the ores are associated with Precambrian metamorphic rocks in general, and the gondites (principally spessertite-quartz rock with or without other manganese silicate) in particular. After Fermor, work in this area has been done by West (18) and recently by a team of geologists of the Geological Survey of India, headed by Straczek (14), and the validity of Fermor's original theory of metamorphic origin of these manganese ores is still unquestioned. The author, in the course of the last two years, has been engaged in the systematic study of the mineralogy of the manganese ores of India and its bearing on their origin. In this connection, the problem of the different types of manganese ore deposits constituting the manganese belt of Madhya Pradesh and Bombay State, which is by far the most important manganese ore-producing region in India, is being investigated initially. The mineralogy and textural relationships of manganese minerals from a type gonditic deposit have been described by the author (13) elsewhere, which gives an idea of the mineralogic composition of the manganese ores of the deposits in close vicinity to the area considered in this paper.

GEOLOGICAL ENVIRONMENT

The Dongari Buzurg manganese mine, which is closely associated with Chikhla and Sitasaongi mines within an area of 15 square miles, is characterized by the following rock formations:

Chorbaoli formation (quartzites, quartz-muscovite schists).
Mansar formation (muscovite-biotite schist locally with staurolite).
Sitasaongi formation (feldspathic quartz-muscovite schist, quartzites).
Tirodi Biotite gneiss.

These rock formations are intercalated with streaks and massive bodies of gondites that in places are composed of spessertite and quartz only. In other cases manganese silicates are present in varying proportions. The manganese ores have two principal modes of occurrence: (1) As massive ore bodies associated with the gondites, and (2) as replacement bodies in the form of nodular, kidney-shaped ores, or cavernous and stalactitic bodies within the schists.

The peculiar and most important feature of the manganese ore deposits of Dongari Buzurg, is their mode of occurrence and mineralogical assemblage, both of which class them as quite different from the other important manganese ore deposits situated close to it. These features, i.e. the mineralogical assemblage, textural relationships and the origin of this interesting ore body, will be dealt with in detail in this paper.

MINERALOGY OF THE ORES

The mineralogy of the manganese ores of Dongari Buzurg has been established mainly by microscopic study of polished sections under reflected light and also by X-ray powder analysis whenever there was any doubt about the conclusive identification of any mineral. The reflecting powers of the different minerals have been determined with the aid of Berek's slit micro-

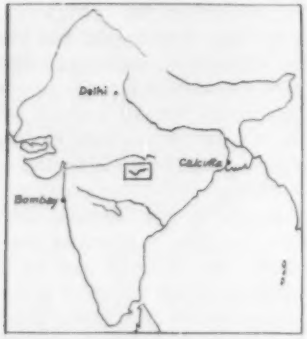

FIG. 1. Index map of India showing location of Madhya Pradesh (now partly acceeded to Bombay) manganese belt. (After Straczek et al., 1956.)

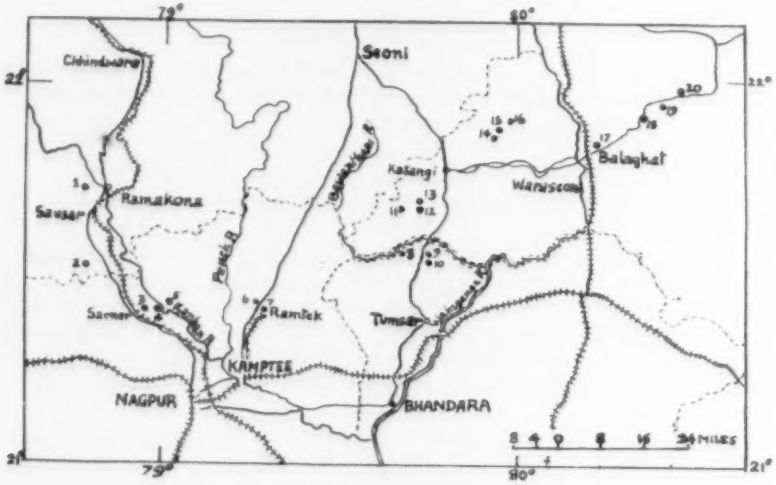

FIG. 2. Map showing location of the major manganese ore deposits of Madhya Pradesh and Bombay, India. (After Straczek et al., 1956.)

List of Deposits

Chhindwara District
1. Kachidhana
2. Gowari Wadhona

Nagpur District
3. Kodegaon
4. Gumgaon
5. Ramdongri
6. Kandri
7. Mansar

Bhandara District
8. Dongari Buzurg
9. Chikhla
10. Sitasaongi

Balaghat District
11. Sitapathor-Sukri
12. South Tirodi
13. North Tirodi
14. Ramrama
15. Shodan Hurki
16. Gulahurkinetra
17. Bharweli
18. Laugur
19. Jagantola-Ghondi
20. Ukwa

photometer using green light, and etching tests were carried out with the minerals to confirm their identification.

The study revealed the presence of the following minerals:

Pyrolusite, manganite, cryptomelane (+ psilomelane), coronadite, jacobsite and braunite. Vredenburgite, the mixed mineral consisting of crystallographic intergrowth of jacobsite and hausmannite, is also present.

Pyrolusite.—Pyrolusite is by far the most abundant mineral in these ores depicting different modes of formation. It occurs as randomly oriented needles, well developed crystals, some twinned (Fig. 8), and colloform bands evidently deposited from colloidal gel. It occurs as primary interstitial mineral in braunites in massive gonditic ores and also as secondary replacement and alteration product of other primary minerals such as jacobsite, braunite and manganite. Both fine and coarse grained varieties are present. The author has found no reason to distinguish between pyrolusite and polianite (cf. Vaux, 17; Strunz, 15) and X-ray powder analysis of all types of pyrolusites exhibit similar pattern.

The color under reflected polarized light is white with a distinct yellow tint and in oil it is pleochroic in these shades. Reflecting power is 33.9 percent in green light in air. Anisotropism is more pronounced in well crystallized large grains in shades of blue-gray, gray and yellow.

For confirmation of the identification of the mineral by microscopic study, scooped out powder of the mineral was subjected to X-ray powder analysis, the results of which are tabulated below:

Etch Reactions

Positive	—$FeCl_3$ in HCl	—Darkens slightly.
-------	—H_2O_2	—Effervesces, surface unaffected.
-------	—$H_2O_2 + H_2SO_4$	—Stains black.
-------	—$SnCl_2$ (Sat.)	—Turns black instantaneously.
Negative	—HCl, HNO_3, KCN, KOH, $HgCl_2$ etc.	

TABLE 1

MEASURED 'd' SPACINGS AND INTENSITIES OF PYROLUSITE
Fe/Mn Radiation

Fleischer & Richmond (1943)		Ramdohr (1956)		McMurdie & Golovato (1948)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
4.08	2						
3.425	2	3.43	S			4.13	3
3.346	1					3.74	2
3.096	10	3.13	SSt	3.14	100		
2.651	0.5					3.11	10
2.537	1					2.648	2
2.396	6	2.41	St	2.42	80		
2.190	3	2.20	S			2.41	9
2.108	4	2.12	M	2.12	50	2.19	3
1.964	4	1.97	M	1.985	70	2.10	8
1.785	1					1.97	4
1.708	1						
1.618	8	1.62	SSt	1.635	80		
1.550	7	1.56	St	1.570	30	1.63	9
And 7 other lines		And 11 other lines				1.55	5

Manganite.—Manganite occurs mostly as fine needles altered to a great extent to pyrolusite, lining the vugs or randomly oriented on a psilomelane base. It occurs both in the colloidal ores and the massive gonditic ores, where it exhibits schistose texture with braunite and pyrolusite.

Manganite is strongly pleochroic from grayish white to brownish gray in polished sections. Reflecting power in green light in air varied from 16 to 20 percent in different grains depending on the orientation of the sections. Extremely strong anisotropism in shades of bluish gray, violet gray, yellowish gray and such lively colors easily distinguish it from other manganese minerals. Cleavage parallel to (010) and (110) often visible.

Etch Reactions

Positive	—HCl (Conc.)	—Attacks the grain with development of etch cleavage.
-------	—$H_2O_2 + H_2SO_4$	—Darkens very slightly.
-------	—$SnCl_2$ (Dil.)	—Darkens very slightly.
-------	—$SnCl_2$ (Sat.)	—Strongly etches and corrodes the grains.
Negative	—HNO_3, H_2O_2, KCN, KOH, $FeCl_3$ etc.	

TABLE 2

MEASURED 'd' SPACINGS AND INTENSITIES OF MANGANITE
Fe/Mn Radiation

Fleischer and Richmond (1943)		Ramdohr (1956)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I
				4.837	1
				4.149	1
3.700	1			3.74	1
3.385	10	3.41	SSt	3.39	10
3.096	1			3.117	1
2.883	1			2.79	1
2.616	9	2.64	M	2.63	5
2.506	2	2.52	S	2.52	3
2.406	6	2.41	M	2.41	8
2.359	0.5				
2.310	0.5				
2.263	7	2.26	M	2.26	6
2.186	3	2.18	M	2.19	6
				2.108	1
1.771	6	1.77	St	1.78	6
1.694	5	1.70	S	1.70	3
1.661	9	1.66	St	1.668	9
1.629	5	1.63	S	1.63	4
				1.55	1
1.493	5	1.50	M	1.50	4
1.428	1	1.43	M	1.43	4
1.424	4				
1.414	1				
1.316	4	1.32	M		
1.287	2	1.29	SS	1.29	2
1.275	1	1.28	SS	1.28	2
1.257	1	1.26	SS	1.26	3
1.239	2	1.24	SS	1.24	3
1.208	1	1.21	SS	1.21	3
And 8 more lines		And 9 more lines			

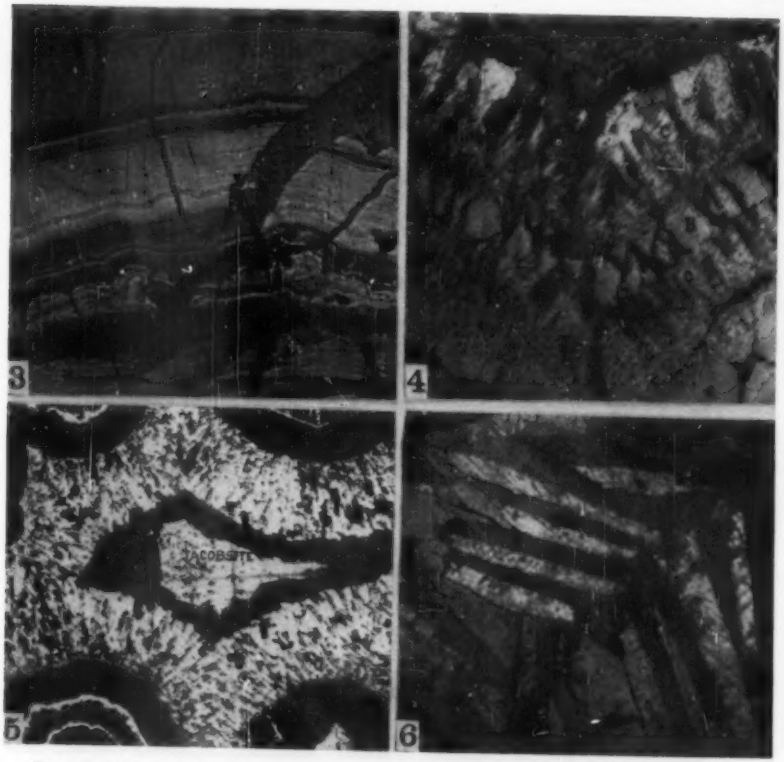

FIG. 3. Colloform texture exhibited by different bands of cryptomelane with slight difference in color and reflectance. The specimen yielded a strong trace of barium and some of the finer lamellae may be psilomelane. The transverse shrinkage cracks are due to contractions. × 160.

FIG. 4. Jacobsite (B) is interbanded with pyrolusite (C) and cryptomelane (A). The fractures are confined mainly to the jacobsite. × 320.

FIG. 5. Needles of pyrolusite and manganite, oriented perpendicular to the vug boundaries. The original jacobsite grain is unaffected in the vug. The texture suggests formation of pyrolusite and manganite needles in open space. × 80.

FIG. 6. Twinning in pyrolusite, simulating herringbone texture. X-nicols. × 320.

Cryptomelane and Psilomelane.—Cryptomelane and psilomelane will be treated in this paper in a group because it was impossible to differentiate the two under the microscope. The minerals are mainly differentiated by X-ray powder pattern and by the barium content in psilomelane. Although many of the specimens examined show the presence of barium as a minor element or as a strong trace, no definite X-ray powder pattern of psilomelane could be obtained. Typical pattern of cryptomelane, however, could easily

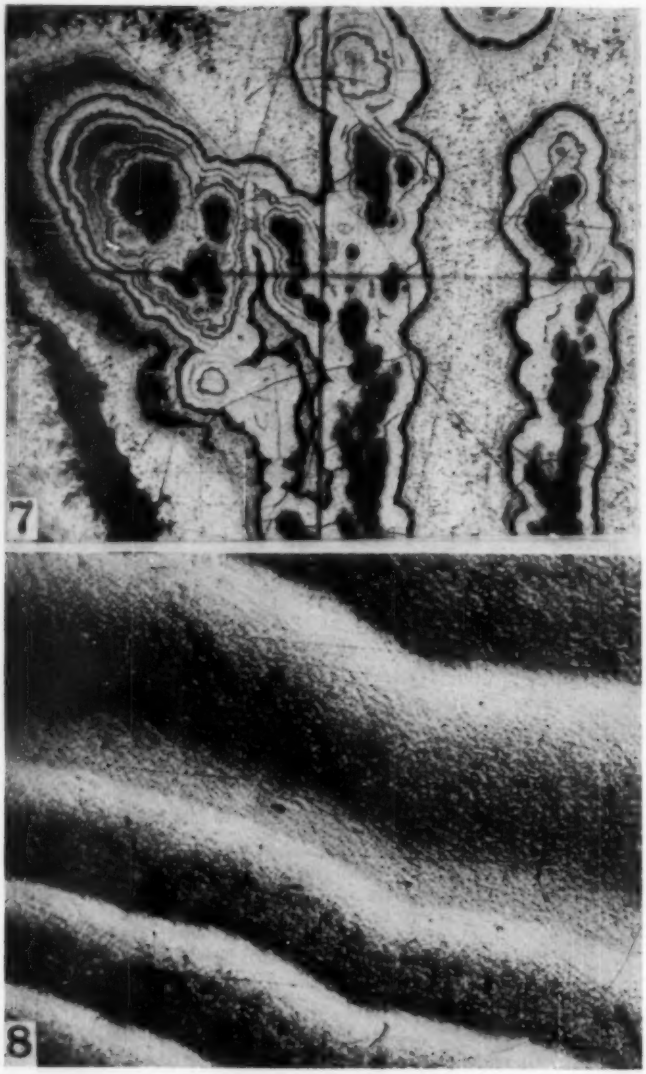

FIG. 7. Colloform texture exhibited by cryptomelane and agate. The alternate bands of white are cryptomelane and those gray to black are agate. × 100.

FIG. 8. Coronadite exhibiting colloform banding. The black and white contrast is due to differential polishing. × 100.

be obtained, and it is concluded that the two minerals are very intimately mixed, with cryptomelane predominating over psilomelane. Since the two have similar modes of occurrence and textural relation, it is convenient and prudent to describe them as a group.

The cryptomelane and psilomelane mainly occur as botryoidal colloform masses along with pyrolusite and less commonly with manganite. They are traversed extensively by lateral shrinkage cracks (Fig. 3). They also form colloform banding and botryoidal aggregates with different varieties of SiO_2

Etch Reactions

Positive	$—HNO_3$	—Stains light brown.
-------	—HCl	—Stains brown, rubs off.
-------	$—H_2O_2$	—Effervesces, surface unaffected.
-------	$—H_2O_2 + H_2SO_4$	—Turns sooty black.
-------	$—SnCl_2$ (Sat.)	—Blackens.
Negative	$—H_2SO_4$, KCN, KOH, $HgCl_2$ etc.	

TABLE 3

MEASURED 'd' SPACINGS AND INTENSITIES OF CRYPTOMELANE
Fe/Mn Radiation

Fleischer & Richmond (1943)		McMurdie & Golovato (1948)		Ramadell (1942)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
6.893	9	6.92	9	6.92	W	6.91	4
4.892	8	4.91	5	4.91	W	5.00	4
3.445	3	3.47	3	3.47	VW		
3.105	10	3.11	10	3.11	M	3.11	7
2.445	3	2.46	2	2.46	VW		
2.387	7	2.40	4	2.40	S	2.39	10
2.305	1						
		2.27	2	2.21	W		
2.183	4						
2.145	5	2.16	3	2.16	W	2.15	6
2.097	1						
1.961	1						
1.917	2						
1.820	5	1.835	2	1.835	M	1.84	3
1.633	4	1.64	3	1.64	W	1.64	3
1.618	4						
1.544	1	1.54	2	1.54	M	1.54	3
Plus 11 more lines				Plus 6 more lines			

(quartz, agate, and chalcedony). Spheroidal rings of silica and cryptomelane are arranged alternately in a concentric form (Fig. 7). Different bands of cryptomelane with slight variation in color and reflecting power, form separate bands in the colloidal ores (Fig. 3).

As already stated, no differentiation of cryptomelane from psilomelane is possible under the microscope, and so the optical characters are also stated as characteristic of the group.

Color under reflected light varies from blue-gray, gray, pale gray and grayish white, some with discernible pleochroism in those shades. Reflecting power in green light in air varies from 28.5 to 30.1 percent. Anisotropism is fairly strong in shades of gray in well crystallized grains, but tends to be very weak in fine-grained aggregates.

Scooped out powder of this group of minerals from polished sections, was subjected to X-ray powder analysis and a good pattern of cryptomelane only was obtained. The results are given in Table 4.

Jacobsite.—This is one of the most abundant minerals in the Dongari Buzurg manganese ores. It has been found in the massive gonditic ores as xenoblastic grains associated with braunite, and excepting when recrystallized,

Etch Reactions

Positive —$H_2O_2 + H_2SO_4$ —Develops etch scratches after long treatment.
- - - - - - - —HF —After long application slightly decolourises the specimen.
Negative —HCl, HNO_3, H_2O_2, $SnCl_2$ etc.

TABLE 4

MEASURED 'd' SPACINGS AND INTENSITIES OF JACOBSITE
Fe/Mn Radiation

Ramdohr (1956)		Miyahisa* (1957)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I
4.81	SS	4.85	3	4.89	4
2.94	St	2.98	5	2.99	6
2.78	SS				
2.52	SSt	2.536	10	2.546	10
		2.434	1	2.436	2
2.09	M	2.104	5	2.11	3
1.71	M	1.723	3	1.725	5
1.61	St	1.624	8	1.627	6
1.48	SSt	1.492	8	1.496	8
		1.426	1		
1.32	S	1.334	1	1.35	2
Plus 7 more lines		Plus 6 more lines			

* The lines for galaxite are omitted.

it never shows hausmannite exsolution lamellae. In the mixed ores anhedral to subhedral grains of jacobsite are abundant, where the later colloidal pyrolusite and psilomelane have engulfed them without showing any replacement relations. The jacobsite is, however, also replaced by, or altered to, pyrolusite and psilomelane on a very limited scale.

The mineral has a non-pleochroic pinkish brown color in the grains devoid of hausmannite, whereas in the vredenburgite it tends to be gray with a tint of olive. The rose brown color is so deceptive that it can be easily confused with magnetite and so the identification was confirmed by X-ray powder analysis (Table 5). The mineral is isotropic between crossed nicols. The reflectivity in green light in air is 19.1 percent.

Braunite.—Braunite occurs mainly in the massive ores and is rarely found in association with the colloidal ores. In the massive ores it coexists both with pyrolusite-manganite-jacobsite assemblage, and also with vredenburgite after recrystallization. It is abundantly replaced by secondary pyrolusite and psilomelane but is not affected by the colloidal manganese dioxide minerals.

The color is gray with pinkish brown or lilac-brown tint. Reflecting power 18.1 percent in green light in air. Anisotropism is weak but distinct.

Etch Reactions

Positive —H_2O_2 —Very slow effervescence, no etching.
------- —$H_2O_2 + H_2SO_4$ —Slow effervescence, darkens slightly.
------- —$SnCl_2 + HCl$ —Stains dark brown.
Negative —HCl, HNO_3, Aqua Regia, KCN, KOH etc.

TABLE 5

MEASURED 'd' SPACINGS AND INTENSITIES OF BRAUNITE
Fe/Mn Radiation

Fleischer & Richmond (1943)		Ramdohr (1956)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I
4.66	1				
4.21	1			4.135	2
3.48	3	3.50	S	3.508	2
3.32	1				
2.96	2				
2.72	6	2.72	SSt	2.721	10
2.68	10				
2.48	1				
2.33	5	2.36	M	2.354	4
2.14	6	2.15	St	2.152	4
1.86	2	1.82	SS	1.879	1
1.83	1				
1.80	1				
1.73	3	1.74	SS	1.74	1
1.65	9	1.66	SSt	1.666	8
1.525	3	1.54	S	1.541	2
1.49	2	1.50	SS	1.509	2
1.46	2	1.47	SS	1.469	2
1.42	8	1.42	St		
1.41	6				
1.37	1	1.36	M	1.364	4
And 12 more lines		And 6 more lines			

For confirmation of the identification of braunite, some powder was scooped out from the polished section and was subjected to X-ray powder analysis (Table 5).

Coronadite.—Coronadite, originally described by Lindgren in 1905 from Coronado vein, Arizona, was questioned as a separate mineral species by Fairbanks (2). But later Orcel (8) confirmed the existence of the mineral

from Bou Tazoult, Morocco, on the basis of which Lindgren (6) re-established his claim. It is isostructural with hollandite and cryptomelane (5).

The mineral occurs as bands in the colloidal manganese ores associated with cryptomelane and psilomelane. It occurs as fine-grained cryptocrystalline bands (Fig. 8) and rarely in medium sized irregular grains. It is pleochroic from grayish white to white, and is strongly anisotropic in shades of gray and brown. Reflecting power in green light in air amounted to 33.7 percent maximum and 31.1 percent minimum in different directions of a strongly pleochroic well crystallized grain.

For confirmation of the identification made by optical criteria, scooped out powder of the mineral was subjected to X-ray powder analysis (Table 6).

Etch Reactions

Positive —HCl (Conc.) —Develops growth lines.
- - - - - - - —H_2O_2 —Effervesces without staining.
- - - - - - - —$H_2O_2 + H_2SO_4$ —Darkens.
- - - - - - - —$SnCl_2$ (Sat.) —Darkens with striations.
Negative —HNO_3, Aqua Regia, KCN, KOH, $HgCl_2$ etc.

TABLE 6

MEASURED 'd' SPACINGS AND INTENSITIES OF CORONADITE
Fe/Mn Radiation

Fleischer & Richmond (1943)		Ramdohr (1956)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I
				6.96	4
3.487	9	3.47	M	3.47	4
3.327	1				
3.3113	10	3.11	SSt	3.13	10
2.387	7	2.39	M	2.40	4
2.198	8	2.19	M/St	2.20	3
2.159	6	2.15	M	2.15	3
1.940	3	1.93	SS	1.937	1
1.83	7	1.83	M	1.83	4
1.74	2	1.73	SS	1.74	2
1.68	3	1.68	SS	1.69	2
1.63	7	1.63	S	1.63	5
1.53	8	1.54	M/St	1.54	5
1.42	1				
1.39	3	1.39	S		
1.37	3	1.37	S	1.37	2
1.36	6	1.35	S	1.35	3
Plus 5 more lines		Plus 6 more lines			

Hausmannite.—Hausmannite has a limited range of occurrence in the Dongari Buzurg ores. It is only found as exsolution lamellae in the vredenburgites present in the massive gonditic ores.

The mineral is distinctly pleochroic from gray to gray white. Reflecting power 21.1 percent in green light in air measured on a very wide lamellae. Anisotropism is strong in shades of yellow and blue.

Etch Reactions

Positive —H_2O_2 + H_2SO_4 —Develops etch scratches, effervesces and darkens.
-------- —$SnCl_2$ (Sat.) —Grains darken.
Negative —HCl, HNO_3, H_2SO_4, KCN, NaOH etc.

TABLE 7

MEASURED 'd' SPACINGS AND INTENSITIES OF HAUSMANNITE
Fe/Mn Radiation

Fleischer & Richmond (1943)		Ramdohr (1956)		S. Roy	
d (Å)	I	d (Å)	I	d (Å)	I
4.851	7	4.92	S/M	4.92	4
3.048	5	3.08	St	3.08	6
				2.98	2
2.867	2	2.87	SS	2.87	3
2.736	9	2.75	St	2.76	8
				2.53	4
2.465	10	2.48	SSt	2.48	10
2.331	5	2.36	M	2.36	4
				2.10	2
2.020	6	2.03	M	2.036	4
				1.967	2
1.809	1	1.82	SS		
1.775	5	1.79	M		
1.686	2	1.70	SS	1.70	3
1.626	1.5	1.64	SS	1.64	2
1.568	6	1.57	St	1.57	3
1.534	8	1.54	SSt	1.54	5
				1.488	3
1.459	1			1.47	4
Plus 15 more lines		Plus 14 more lines			

TEXTURAL RELATIONSHIPS AND THEIR INTERPRETATION

As already described, the Dongari Buzurg manganese ores are characterized by different modes of occurrence and mineralogical assemblage, and the general textural relationships also vary with them. In describing the texture of the ores, therefore, three broad divisions have been made according to the mode of occurrence of the particular ore suites:

(i) The hard massive ores associated with the gondites.
(ii) The cavernous, banded, kidney-shaped and stalactitic ores as replacement deposits in mica schists.
(iii) A mixture of the hard, massive, gonditic ore and the cavernous, kidney-shaped replacement ores.

These will now be dealt with separately.

Hard Massive Ores Associated with the Gondites.—These are mainly braunite-manganite-jacobsite-vredenburgite ores with minor amount of pyrolusite and cryptomelane. This typically metamorphic ore suite can be broadly divided into two divisions according to primary mineral assemblage and texture: 1) the pyrolusite-manganite-braunite-jacobsite assemblage with a typical schistose texture (Fig. 9) the braunite-vredenburgite assemblage

with coarse intergranular texture (Fig. 10), originating evidently from recrystallization and rearrangement of earlier minerals. These different assemblages of ore minerals have been traced in different lodes associated with the gondites. The texture of these ores, as a whole, is typical of gonditic derivation, originating from metamorphism of manganiferous sediments, similar to that described by the author from Tirodi (13), which is a type area for gonditic manganese ores and which incidentally lies in close vicinity of the area under consideration in this paper.

A noteworthy aspect of the textures of these ores is that in the schistose pyrolusite-manganite-braunite-jacobsite ore, no exsolution of hausmannite in jacobsite is observed, whereas in the recrystallized ores such crystallographic intergrowths (vredenburgite) are abundant. This is due, according to the

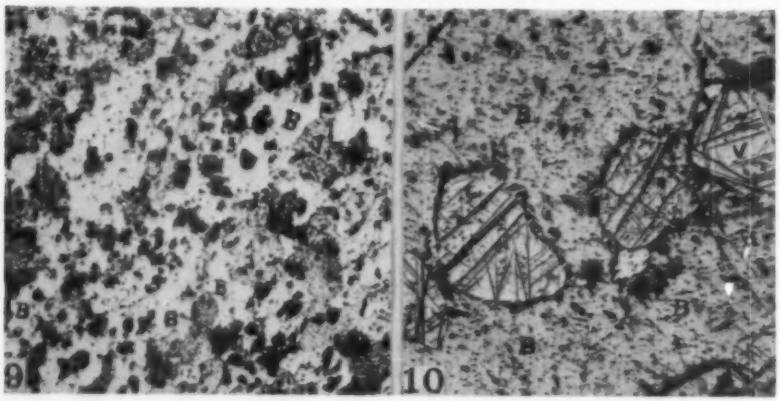

FIG. 9. Schistose texture exhibited by braunite-jacobsite-manganite-pyrolusite assemblage. The minerals aligned are braunite (B) and jacobsite (J). × 175.

FIG. 10. Coarse grained vredenburgite and braunite formed by to recrystallization. The hausmannite lamellae in vredenburgite etched black. × 90.

author, not to compositional variation, but presumably to lack of proper temperature attained in the schistose ores. It is evident that the exsolution of hausmannite in jacobsite is related to recrystallization at an elevated temperature when sufficient time was allowed (as shown by large grain size). According to Edwards (1, p. 39), such exsolution can be due to recrystallization. Another interesting fact is that neither primary pyrolusite nor manganite, coexist with the vredenburgite, indicating a higher pressure-temperature condition beyond the stability region of these minerals, but they occur abundantly with hausmannite-free jacobsite.

Supergene cryptomelane and pyrolusite have replaced braunite, vredenburgite, and manganite abundantly. No evidence of colloidal deposition was noticed in the gonditic ores themselves except where they are invaded by the later colloidal gel.

Cavernous, Banded, Kidney-shaped and Stalactitic-botryoidal Ores as Replacement Deposits in Schists.—These consist mainly of cryptomelane-psilomelane-coronadite-pyrolusite-manganite ore invariably associated with colloidal deposits of quartz, agate and chalcedony. The ores exhibit typical colloform texture in which cryptomelane, psilomelane, and coronadite show spheroidal or banded appearance. In most cases alternate concentric bands of cryptomelane, psilomelane, pyrolusite and silica are found. Regular colloform banding of a different generation of psilomelane, with slight variation in color and reflectance, is quite common (Fig. 3). Pyrolusite and manganite are commonly present as needles lining the vugs (Fig. 5) and also scattered in irregular directions on a base of pyrolusite, generally indicating deposition in open space.

Effects of supergene alteration in the colloidal ores are also general where manganite is abundantly altered, commonly pseudomorphically, after pyrolusite (Figs. 13, 14). Cryptomelane also, at places, is altered to pyrolusite.

The Mixture of Hard, Massive, Gonditic Ore and Colloidal Replacement Ore.—In a number of specimens taken from the contact of the colloidal replacement ore body and the massive ore associated with the gondites, interesting associations of manganese minerals have been found. Considerable jacobsite, free of hausmannite, has been found in these ores, and has rendered the otherwise mainly manganese dioxide ore strongly magnetic. The texture exhibited by the cryptomelane-psilomelane-pyrolusite-manganite-assemblage, which are the important minerals in this group, is typically colloform, with concentric bands (Figs. 3, 4, 7, 8) and radiating fibrous crystals (Fig. 5) commonly exhibiting twinning (Fig. 6). Jacobsite is inset in regular pattern in these minerals. Commonly the jacobsite is surrounded and enveloped by minerals of colloidal origin, but practically no replacement relation is observed (Figs. 11, 12). The later cryptomelane-psilomelane-pyrolusite-manganite group of minerals have moulded themselves against the already existing jacobsite and minor braunite. In large grains of pyrolusite and manganite, jacobsite is included. The cleavage lines, crossing the former minerals have stopped at the jacobsite border and continued beyond it unaffected (Fig. 12). It can be postulated that the pre-existing jacobsite and braunite are members of the high-temperature gonditic assemblage of ores, which were invaded later by colloidal gel depositing the other low-temperature mineral assemblage. The jacobsite and braunite were not affected by the process but remained as inclusions in the invading cryptomelane-psilomelane-pyrolusite-manganite grains.

An attempt may now be made to trace the paragenetic relationship of the individual or group of minerals. As the field relations or ore texture suggest, the massive gonditic ore body composed of braunite, jacobsite, vredenburgite, manganite, and pyrolusite was formed initially by the metamorphism of early manganiferous sediments. In these ores, two principal phases can easily be recognized, namely, the earlier braunite-jacobsite-manganite-pyrolusite phase, where the minerals exhibit well developed schistosity and no evidence of recrystallization, and the second later phase where considerable recrystallization has taken place. In this, oriented lamellae of hausmannite have exsolved

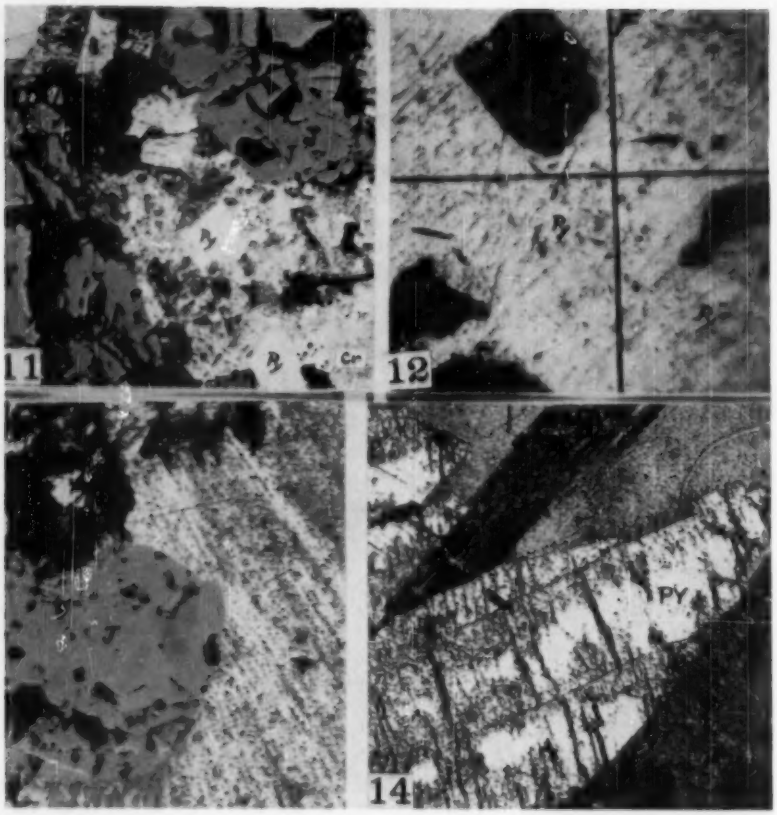

FIG. 11. Contact of jacobsite (J) and later colloidal pyrolusite (Py) and cryptomelane (+ psilomelane). There is no replacement relation between jacobsite and colloidal minerals. × 270.

FIG. 12. Jacobsite (J) grain included in pyrolusite (Py). The cleavage lines in pyrolusite continue beyond jacobsite unaffected. × 360.

FIG. 13. Pyrolusite replacing manganite in the cleavage direction while a jacobsite grain (J) protrudes; pyrolusite—white, manganite—gray. × 360.

FIG. 14. Pseudomorphic replacement of manganite (dark gray) by pyrolusite (white). The needles of manganite are oriented in cryptomelane (Cr) base. × 580.

in jacobsite and no trace of primary manganite or pyrolusite could be found. It is difficult to decipher the individual paragenetic history of the first group of minerals excepting that primary pyrolusite formed in the interstices of braunite. No replacement relation have been found between braunite, jacobsite or manganite. In the second phase, the grain size of the minerals tend

to be coarser and evidence of recrystallization is present throughout the section; exsolution of hausmannite in the octahedral direction of jacobsite is induced and the pyrolusite and manganite are no longer stable. Secondary pyrolusite and psilomelane were formed much later and replaced all the primary minerals abundantly in both the mineral assemblages.

The cavernous, banded, and kidney-shaped manganese ore body is much later than the massive gonditic ores as suggested by the replacement relations they exhibit with the mica schists and the ore textures of the mixed ores of these two types. It is difficult, however, to single out the colloidal minerals and consider them individually in the paragenetic sequence, as almost all of them, namely, cryptomelane, psilomelane, pyrolusite, and coronadite, occur as concentric rings or colloform bands and do not show any replacement relation between them. Needles of pyrolusite and manganite, oriented perpendicular to the banding of cryptomelane-psilomelane or to the vug boundaries, are probably a trifle later in deposition. Secondary pyrolusite formed much later at the expense of manganite and psilomelane.

In reviewing the texture and paragenesis of these ore minerals, the role of jacobsite should be emphasized. It occurs abundantly in the gonditic ores, in vredenburgites or as individual grains free of hausmannite. There is a sharp change in color and to a lesser degree in reflecting power of the mineral, which is olive gray in intergrowth with hausmannite, and rose brown (like magnetite) in individual free grains. In the colloidal ores also, jacobsite, free of hausmannite, is irregularly scattered in and engulfed by later colloidal psilomelane-cryptomelane or pyrolusite and here also a typical rose brown color is exhibited.

The presence of irregularly scattered grains of jacobsite in later colloidal manganese dioxide minerals can be explained by the colloidal invasion in the earlier schistose ore, which was less compact than the recrystallized gonditic ore bands. A singular peculiar occurrence of jacobsite, interbanded with cryptomelane and pyrolusite (Fig. 4), however could not be explained, excepting by more ore less contemporaneous deposition from a colloidal "gel," though such low-temperature of formation for jacobsite is rather improbable.

On the basis of textural relationships and their interpretation, the following paragenesis has been drawn up for the manganese ore bodies of Dongari Buzurg:

ORIGIN OF THE ORE BODIES

An attempt to trace the origin of the manganese ore bodies of Dongari Buzurg may be made by interpreting the data previously given. Straczek et al. (14) attributed a primary origin to the gondites and the associated ore bodies by metamorphism of manganese sediments and argued that the abundant manganese dioxide minerals extending to 400 feet below the original surface outcrop and 250 feet below the present water table, have been formed by supergene oxidation of gondite and braunite. They envisaged an ancient weathering cycle that brought about the supergene alteration and accumulation of this huge deposit of manganese dioxide ores, which were later somewhat enriched by the present weathering cycle.

While the present author corroborates Straczek et al. (14) as to the primary metamorphic origin of the gonditic ores, his findings do not support the origin advocated by them for the cavernous, banded, kidney shaped, botryoidal-stalactitic ores purely by oxidation and supergene enrichment. These ores, composed chiefly of manganese dioxide minerals, replace the schists abundantly and gondites to some extent, and are accompanied by considerable amount of silica in the form of quartz, agate, and chalcedony. Cryptomelane and psilomelane form alternate concentric bands with agate or chalcedony in colloform deposition (Fig. 7). The needles of pyrolusite and manganite oriented perpendicular to the vug boundaries or concentric rings of colloform psilomelane or cryptomelane, point to deposition in open space; shrinkage cracks, traversing laterally the concentric rings (formed evidently by surface tension in the original colloidal gel) of psilomelane and cryptomelane, suggest contraction during consolidation and deposition. Also the characteristic spherical nodules of psilomelane and cryptomelane, during close contact with one another, deformed each other mutually without breaking, which is convincing evidence that at the moment of their origin, they were non-rigid bodies, i.e., "gels."

All of this evidence indicates that an original colloidal nature of the material that gave rise to the botryoidal, kidney-shaped and banded ore bodies, is the most probable explanation. The colloidal gel evidently invaded the highly foliated schists, taking advantage of the foliation, porosity and the fault planes. The gondites and massive ore bodies are also invaded by them and some sort of solution and leaching within the gondites has to be envisaged prior to the deposition. It is suggested that silica in the gondites might have been leached out and the colloidal gel was enriched with it.

Although some supergene enrichment of the massive gonditic ore by oxidation and weathering has taken place, as is evidenced by jacobsite, braunite, and hausmannite (in vredenburgite) altering to secondary pyrolusite and psilomelane, the total effect is so negligible that any substantial enrichment in the ore body is unexpected. In the mixed colloidal and massive gonditic ores, irregular grains of jacobsite are present where the colloform pyrolusite and psilomelane and cryptomelane have either included them or have moulded themselves along the boundary of the jacobsite. Thus, evidently the forma-

tion of the manganese dioxide ore was brought about by invading colloidal gel rather than just by enrichment in situ due to supergene oxidation or weathering.

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SCIENTIFIC COMMUNICATIONS

A NOTE ON THE STRUCTURE FILMING PROPERTIES OF BOURNONITE IN POLISHED SECTIONS

A. P. MILLMAN AND J. A. VALVANO

Incidental to a study of the application of the selective iridescent filming technique in the examination of polished sections of ore minerals (1), it was observed that in the case of bournonite, brilliant colored bands indicating twin lamellae and growth zones were developed by filming, these features not being detectable in polarized light or only very weakly so. Comparable results for bournonite have previously been reported by Gaudin (2) using a similar technique, and by Head and Loofbourow (3) who employed an azolitmin staining reagent.

The technique consists of creating on the polished surface of the mineral, a transparent thin coating by means of immersion in a suitable liquid oxidizing medium. The thickness of the film produced depends on (a) mineral species, (b) crystal orientation, (c) reagent concentration, (d) immersion time, and (e) temperature of the reagent. After immersion, the polished section surface is dried and then examined in white light under a reflecting microscope. Reflection takes place from both the upper and lower surfaces of the film, producing phase difference and Newtonian colors, the actual hue produced being dependent on the film thickness and other characteristics.

PROCEDURE AND RESULTS

The polished section containing bournonite is carefully cleaned free from grease or oil by washing with methyl alcohol and rubbing with Kleenex tissue, and then dried by means of a spray of acetone. Filming is then carried out by immersion of the section for 40 to 60 seconds in a beaker containing a CrO_3-HCl solution at room temperature, (19–22° C). The filming solution is prepared by dissolving 10 g of CrO_3 in 350 ml of water and adding 75.6 ml concentrated HCl. Immediately after removal of the specimen from the bath, it is washed in distilled water, and dried by spraying in acetone. Examination of the iridescent film is then carried out on the reflecting ore microscope, with a heat-absorbing filter at the light source to prevent deterioration of the film.

Specimens of bournonite from Herodsfoot Mine, Cornwall, and Shallee Mine, Eire, were examined. In both cases, parallel twin lamellae, growth bands and twinned aggregates revealed their presence in brilliant iridescent orange, yellow, purple and blue colors. With oil immersion, the intensity of

the colors was considerably reduced. In ordinary and polarized light (XN), little could be seen of any of these structures before filming.

In the Head and Loofbourow test for bournonite (3), azolitmin is used as a staining reagent at 95° C producing similar effects to those obtained with the filming solution. The use of azolitmin is therefore not essential for the formation of these characteristic patterns, and they are more readily obtained with the chromic oxide-hydrochloric acid filming solution at room temperatures.

APPLICATIONS

In their study of the filming properties of "feather ores" and similar minerals, as well as other common ore minerals, the writers (1) have shown that the filming method is unreliable as a mineral determinative technique, since the colors obtained under standardized conditions for any particular mineral species may vary with (a) composition and locality of the specimen, (b) growth zoning, and (c) crystal and twinning directions. However, these adverse factors can be turned to advantage in the interpretation of ore textures, since intergrowths, zoning, twinning deformation and ore fabric characteristics are often not visible even under polarized light, and these very structures are enhanced by selective iridescent filming. The procedure may be described as "structure filming," analogous with structure etching effects produced by other types of reagents.

Department of Mining Geology,
Royal School of Mines, London,
Sept. 23, 1959

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2. Gaudin, A. M., 1938, Identification of sulphide minerals by selective iridescent filming: Tech. Publ. Amer. Inst. Min. Engrs. no. 912 (Min. Technol., N. Y., March), 16 p.
3. Head, R. E., and Loofbourow, R. W., 1934, A microchemical method for the determination of bournonite: Econ. Geol., v. 29, p. 301–305.

Economic Geology
Vol. 54, 1959, pp. 1577–1578

DISCUSSIONS

STRUCTURAL HISTORY OF THE BEAVERLODGE AREA

Sir: J. A. Chamberlain cleverly works out the net-slip for the St. Louis-ABC fault (ECON. GEOL., vol. 54, no. 3, p. 478–494). However . . .

(i) The structural history of one fault is not, by itself, a structural history of the whole Beaverlodge area. (ii) Two faults occur on the other side of Beaverlodge Lake on line with the St. Louis fault. Both show right-handed movement of 1,000 to 1,200 feet and both are described in a paper of more modest title (2). What examination, if any, was made of these faults? (iii) What evidence exists for the "reactivation of stresses" and the "late change in direction of force suggested by cross-folding" of Table 1? (iv) The true Athabasca formation does not occur in the Beaverlodge area. A footnote drawing attention to the paper by Gussow (1) published in January of this year would have been appreciated.

PATRICK ARTHUR HILL

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1. Gussow, William C., 1959, Athabasca formation of western Canada: Geol. Soc. America Bull., v. 70, p. 1–18.
2. Hill, Patrick A., 1956, Geology of the Pitch Group, Beaverlodge Lake, Sask.: Precambrian, v. 29, no. 1, p. 6–10.

THE APPLICATION OF WHITE SPIRIT IN FIELD DITHIZONE COLORIMETRY

Sir: Following the work by Holman (4) at the Geochemical Prospecting Research Centre, Imperial College, the use of white spirit in dithizone methods was first extended to the determination of cold extractable zinc, with considerable success. It had been observed that the solubility of dithizone and its metal complexes is appreciably less in white spirit than in the more conventional solvents, and this property was exploited by various workers at the Research Centre for the determination of lead. A mono-color technique was developed that was superior to the method of Bloom and Crowe (1) since it obviated the need for a preliminary phase separation.

In the meantime, white spirit was being tested as a substitute for carbon tetrachloride in the determination of the total copper and total zinc contents of soils, sediments, and rocks. The work in this connection does not fully accord with the experience of Hill (3). Dithizone in white spirit solution is readily converted into diphenylthiocarbadiazone, the ease with which this

takes place being dependent upon the quality of the solvent. The purification of white spirit by shaking with concentrated sulfuric acid is an undesirable operation, and it is frequently necessary to follow this by a distillation. Even so, the resulting solvent would vary considerably in its suitability for dithizone tests, although any one drum of white spirit would be consistent within itself. An additional disadvantage, particularly for field work, is the necessity to use a stock solution of dithizone in chloroform, since again the stability of dithizone is very much dependent upon the quality of this solvent.

Hill's statement that white spirit appears to be superior to xylene and other lighter than water solvents does not agree with our findings at Imperial College. Both benzene and toluene solutions of dithizone are very much more stable than those in white spirit. In commercial quality (as nitration grades) their cost is the same as for white spirit, but it is probably necessary to purify by distillation. The crystallizable grade of laboratory reagent is recommended for benzene, and the sulfur-free grade for toluene. If the low-flash point and freezing point of benzene are considered to be a disadvantage, then toluene may be substituted. Both these solvents are readily available, and they require identical test conditions for the determination of copper, zinc, and lead.

Benzene as a solvent for dithizone has been in use at the Geochemical Prospecting Research Centre since the beginning of 1957. The procedures for the determination of copper and zinc (both total and cold-extractable) are similar to those using carbon tetrachloride or white spirit. Lead is determined by a mixed color procedure that is based upon the method used by Bureau de Recherches Géologiques, Géophysiques et Minières (2). Many thousands of samples have been analyzed for these three elements, and benzene has proved to be far preferable to white spirit as a solvent for dithizone, both in the field and in the laboratory, with toluene being equally satisfactory.

R. E. STANTON

REFERENCES

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2. Bureau de Recherches Géologiques, Géophysiques et Minières, 1957, Methods of analysis used in microchemical prospecting by the B.R.G.G.M., p. 1–22.
3. Hill, V. G., 1959, The application of white spirit in field dithizone colorimetry: Econ. Geol., v. 54, p. 310–312.
4. Holman, R. H. C., 1956, A method for determining readily-soluble copper in soil and alluvium—introducing white spirit as a solvent for dithizone: Inst. Min. Met. Trans., v. 66, p. 7–16.

Economic Geology
Vol. 54, 1959, pp. 1579–1592

REVIEWS

SHORT REVIEWS OF NEW RUSSIAN BOOKS

Geokhimiya Redkikh Elementov v Svyazi s Problemoi Petrogenezisa. [The geochemistry of rare elements in relation to problems of petrogenesis.] Pp. 167. Academy of Sciences, Moscow, 1959. Price, 10r. 75k.

A geochemical symposium concerned principally with discussions on the tenor of the rarer elements in igneous rocks in relation to problems of petrogenesis was held at the Vernadsky Institute of Geochemistry in Moscow in December 1957. Earl Ingerson (U.S.G.S.) and L. H. Ahrens (Capetown University) took part. The report contains eleven principal papers on the geochemistry of Sc, V, TR(RE), Zr, Hf, Nb, Ta, Be, Rb, Tl, Pb, Zn and Mo in igneous rocks, followed by 25 pages of general discussion in which some 27 authors took part. The value of the publication is not enhanced by the exclusion of all bibliographical references to earlier works.

Autigennye Mineraly Osadochnykh Porod. [Authigenic minerals of the sedimentary rocks.] By G. I. Teodorovich. Pp. 223. Academy of Sciences, Moscow, 1958. Price, 9r. 40k. (paper covers).

Although much of this booklet is taken up with mineralogical information readily available elsewhere, it also contains useful discussions on the mode of development of the principal authigenic minerals in sediments, with references to the copious Soviet literature. Authigenic zeolites (eight species) are much more widely recognized in Russian strata than anywhere else. In all, around 150 authigenic mineral species are dealt with.

Novoe v Metodike i Tekhnike Geologorazvedochnykh Rabot. [New methods and techniques of geological-prospecting work.] Pp. 423. Gostoptekhizdat, Moscow, 1958. Price, 19r. 80k.

Of two dozen articles, seven are concerned with various aspects of geochemical and alluvial prospecting for metals, thirteen with new geophysical methods, and four with drilling techniques. One gets the general impression that, relative to western standards, the geochemical work is further advanced than the geophysical studies.

Otechestvennye Geologii. [Geologists of our homeland.] By S. S. Kuznetsov. Pp. 193; figs. 26. Gospedagogizdat, Moscow, 1958. Price, 3r. 50k.

A series of popularized biographies of distinguished Russian geologists, written for older school-children and for elementary students. Separate chapters cover the life and work of A. P. Karpinskii, I. D. Cherskii, A. A. Inostrantsev, F. Yu. Levinson-Lessing, P. A. Zemyatchenskii, A. P. Pavlov, A. D. Arkhangelskii, I. M. Gubkin, and V. A. Obruchev.

Ocherki po Istorii Geologicheskikh Znanii. [Essays on the history of geological knowledge.] No. 7. Pp. 227. Academy of Sciences, Moscow, 1958. Price, 11r. 30k.

The principal contribution to this collection of historical studies is an article by Belyankin and Tsvetkov on the development of experimental mineralogy and petrology in Russia (42 pp., with a 70-page bibliography). Another paper, with a good literature list, is concerned with the history of mineragraphy (ore microscopy) in the U.S.S.R.

Izbrannye Trudy. [Collected works] of L. S. Berg. Vol. I, pp. 395. Price, 26r. 25k. Vol. II, pp. 426, 1958. Price, 28r. 45k. Academy of Sciences, Moscow.

Although Berg was primarily a geographer his publications have a catholicity of range, from studies in natural history to works on sedimentary ore deposits. The first volume of this collection of his writings, mainly on the history of science, includes among many other essays such topics as "Charles Darwin as a zoologist," "The first Russians in England" (1553), and "The Russian discovery of N.W. America" (1648). The second volume, comprising his geographical works, reprints his publications on the Ural bauxites and other papers on the sedimentary rocks.

Shchelochnye Granity Kol'skogo Poluostrova. [Alkalic granites of the Kola peninsula.] Pp. 374. Kola filial, Academy of Sciences, Moscow-Leningrad, 1958. Price, 23r. 75k.

This symposium comprises a dozen papers on the geology and petrography of different massifs of alkalic granite in Kola, with four contributions on the general problems of the petrology and petrochemistry of these granites. The latter works contain a wealth of analytical detail.

Razvedka i Razrabotka Poleznykh Iskopaemykh. [The prospection and exploitation of useful minerals.] Pp. 250. Gostoptekhizdat, Moscow. Price, 20r. 30k.

An "All-Union" conference on the application of radioactive isotopes in the mineral industry was held in 1957 at the behest of the Academy of Sciences. The 34 papers in this report of the meetings are mostly concerned with techniques of gamma and neutron logging of boreholes in the search for oil and in coal-field correlation. Other topics discussed include: aeroradiometric surveying as a tool in geological mapping; neutron methods in prospecting for and in the analysis of boron minerals; radioactivity techniques of exploration for potash salt deposits; the use of radioactive isotopes in the study of explosives in mines; and their use as a control in the cleaning of coal.

Vysshee Obrazovanie i Podgotovka Nauchnykh Kadrov v SSSR. [Higher education and training for scientific personnel in U.S.S.R.] By K. T. Galkin. Pp. 176. Sovetskaya Nauka, Moscow, 1958. Price, 7r.

A historical review is given of the systems of higher education for scientists maintained in Russia from about 1800 onward. About half the book deals with the pre-Revolutionary period. In the five years 1951–55 there graduated 1,028 "candidates" (= Ph.D.'s) and 150 "doctors of science" in geology and mineralogy.

Averaged over all sciences, at the time of their final examination 86% of the candidates were aged over 30 and 39% over 40 years; of the doctors, 85% were aged over 40 and 37% over 50 years.

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
Aug. 15, 1959

Ground Water Hydrology. By DAVID K. TODD. Pp. 336. John Wiley & Sons, New York, 1959. Price, $10.50.

Much of the water supply of the world comes from underground water, and with the growth of population, industrialization, and the reaching back by metropolitan areas into rural areas for surface water supplies, more underground water will be sought in the United States. This up-to-date book is therefore very timely.

Its 14 chapters adequately cover both broad and detailed features of ground water. They take up occurrence, movement, hydraulics, wells, fluctuations, quality, basin-wide development, surface and underground investigations, recharge, sea water intrusion, legal aspects, and modal analysis. The book tells how to locate a ground water supply, construct a well, determine how much water it will yield, how much a well can be pumped, and problems of pollution.

The book is full of information for the geologist, the farmer, the industrialist, and water supply utilities.

Geochemical Methods of Prospecting and Exploration for Petroleum and Natural Gas. By A. A. KARTSEV, Z. A. TABASARANSKII, M. I. SUBBOTA, and G. A. MOGILEVSKII. English translation edited by P. A. WITHERSPOON and W. D. ROMEY. Pp. 349; figs. 151. Univ. of California Press, 1959. Price, $12.50.

The Russians in the last 30 years have developed an impressive number of geochemical methods for prospecting for oil and gas. This information has been gathered by the members of the Gubkin Institute of Petroleum and Gas Industry and the Research Institute of Petroleum Geology, in Moscow, and forms the basis of this book. These methods deal with hydrocarbon gases, bitumen, salts, and bacteria.

There are 15 chapters dealing with such subjects as the geochemistry of petroleum formations, classification of prospecting methods, geochemistry of gases, gas surveys, logging, bitumen methods, hydrochemical methods, water-gas surveys, soil salt, oxidation-reduction potential, microbiological, and the role of geochemical methods in petroleum prospecting.

Apparently geochemical methods have been effective in prospecting for and actually finding oil in Russia, but the more advanced methods used in the western hemisphere and in the Middle East have been even more effective. However, some of their illustrations and logs are illuminating.

As prospecting for oil becomes more difficult perhaps some of these methods may become of interest to non-Russian prospectors for oil. However, it appears that the Russian procedures are beginning to catch up with North American procedures used many years ago and supplanted by much more modern methods of prospecting for oil, much of which has not yet crept into the literature.

This book is interesting in showing modern Russian trends and in contrast to what is going on elsewhere in the outside world.

Atmospheric Chemistry of Chlorine and Sulfur Compounds. Edited by JAMES P. LODGE, JR. Pp. 127. Geophysical Mon. No. 3, American Geophysical Union, Pub. No. 652, Washington, D. C., 1959.

This volume presents the results of a symposium held in Cincinnati, Ohio, Nov. 4–6, 1957, under the joint sponsorship of the U. S. Public Health Service, and the American Geophysical Union, aided by a grant from the National Science Foundation.

It consists of 29 articles by 36 authors. There are four sections: Analytical Methods (8 papers), Field Techniques and Engineering Controls (4 papers and discussions), Atmospheric Concentrations (8 papers and discussions), and Atmospheric Budget (4 papers). The subjects covered are analytic methods and determinations of chlorine and sulfur, techniques and controls for SO_2, sulfur and chlorine compounds in the atmosphere, kinetics, health, rainwater distribution, marine winds, and geochemistry.

The volume brings together modern thought in the fields of cloud physics, atmospheric chemistry and air pollution.

Principles of Geology, 2nd Edit. By J. GILLULY, AARON C. WATERS, and A. O. WOODFORD. Pp. 534, figs. 335. W. H. Freeman and Co., San Francisco, Calif., 1959. Price, $7.50.

This second edition follows the first after 8 years. The advances in geology during that period are incorporated in this new edition. Each chapter has been rewritten and reorganized. An entirely new chapter has been added on sedimentary rocks and their environments of deposition. The chapter on Strata, Fossils, and Time has been expanded as have the sections dealing with metamorphic rocks and metamorphic processes. Many new and excellent illustrations have been incorporated.

The general organization of the book is little changed, except for the reorganization of the content of individual chapters.

Concise Dictionary of Science. By FRANK GAYNOR. Pp. 546. Philosophical Library, New York, 1959. Price, $10.00.

The author of this dictionary is the Editor of the Encyclopedia of Atomic Energy and a science contributor to the Encyclopedia Brittanica.

This dictionary provides definitions of terms and concepts in many fields of science, even though the title page states "Physics-Mathematics-Nucleonics-Astronomy-Chemistry." It defines many of the terms used in geology, as well as other sciences, but it is not a dictionary of geology.

The book appears at a time when science is much in the forefront and an up-to-date dictionary of science terms will be welcomed by everyone, both scientist and layman.

Economics of the Mineral Industries—A Series of Articles by Specialists. Edited by EDWARD H. ROBIE. Pp. 755. Amer. Inst. Min., Metall., and Petroleum Engrs., New York, 1959.

This book is another volume in the well known Seeley W. Mudd Series of the A.I.M.E. and is prepared as a memorial to Harvey S. Mudd through the Seeley W. Mudd Memorial Fund. It is meant to provide "a reference for professional use and a textbook for advanced study. To the extent compatible with these objectives, the education of semiprofessionals and the public is a desirable objective."

There are 18 chapters written by 38 authors, all specialists in their fields. They cover the subjects of the significance of mineral industries in the economy, and their distinctive features, titles and tenure, valuations, cost of acquiring and operating mineral properties, financing, bank loans on oil and gas, marketing, accounting, supply and demand and taxation. Other broader subjects include the relation of minerals to national and international affairs, government aid, conservation, labor-management, research, money and credit, nuclear energy, and finally "Minerals in Man's Future." Extended bibliographies accompany each chapter.

As will be seen, this is a broad range of subject matter and supplies a vast amount of authoritative information for anyone interested in the economics of the mineral industry.

Researches in Geochemistry. Edited by PHILIP H. ABELSON. Pp. 511. John Wiley & Sons, Inc., New York, 1959. Price, $11.00.

The rapidly growing interest in geochemistry stimulated the Geophysical Laboratory of the Carnegie Institution of Washington to organize a seminar series in geochemistry, held at the Geophysical Laboratory and at the Department of Geology of The Johns Hopkins University. Twenty-three seminars were held, conducted by twenty-five authorities. The content of the seminars, along with the results of discussion, and some revision by the authors are presented in these twenty-three essays under the editorship of Dr. Abelson, Director of the Geophysical Laboratory in Washington. The authors were drawn from the Geophysical Laboratory, the U. S. Geological Survey, the U. S. Atomic Energy Commission, Mellon Institute, Scripps Institute, Argonne Laboratory, and the Universities of Pennsylvania State, Groningen (Netherlands), California Institute of Technology, Harvard, Chicago, California, Stanford, and Massachusetts Institute of Technology.

Each essay reviews present research in each author's field, giving some of his own contributions and a selected bibliography.

The various topics give a good idea of current research in field. These topics are:

Nuclear Geology:	Libbey	Tritium
	Epstein	Oxygen isotopes
	Ault	Sulfur isotopes
	Reed	Activation analysis
Geochemistry:	Tilson and Davis	Ancient dating
	deVries	C^{14} developments
Ore Solutions:	Krauskopf	Magmatic gas phase
	Barton	Chemical of ore depositsion
	Kullerud	Sulfide geothermometry
	Hawkes	Geochemical prospecting
Geochemistry of Organic Substances:	Abelson	Organic geochemistry
	Hanson	Petroleum
Low-temperature Processes:	Arrhenius	Deep-sea sedimentation
	Garrels	Low-temperature reactions
	Keith and Degens	Marine vs. non-marine
	Milton and Eugster	Green River minerals

Metamorphism:	Thompson	Metasomatism
	Boyd	Amphiboles
	Eugster	Iron minerals
Carbonates:	Goldsmith	Geochemistry of
Short-range Ordering:	Chayes	diffraction effects
Earth's Interior:	MacDonald	Constitution of high-pressure
	Clark	phenomena

From the above topics, subjects, and authors it will be seen that the coverage is comprehensive and authoritative. The volume is an excellent conception and has been well carried out. It will serve as an outstanding reference to students of earth sciences and chemists.

BOOKS RECEIVED

JOHN E. COTTON AND CYRUS W. FIELD

Bibliography of the Stable Isotopes of Oxygen (O^{17} and O^{18}). Compiled and edited by DAVID SAMUEL and FRITZ STECKEL. Pp. 224. Pergamon Press, New York, 1959. Price, $7.50. *A complete record of papers published up to the end of 1957 arranged as an author and subject index.*

Beaches and Coasts. C. A. M. KING. Pp. 387. St. Martin's Press, Inc., London and New York, 1959. Price, $14.50. *An interesting book on waves, tides, and winds and their effects on movement and sorting of beach materials and the development of beaches and coast lines, beach profiles, sea-level changes, and the marine cycle.*

Lessons in Seismic Computing. M. M. SLOTNICK. Pp. 268; figs. 123. Society of Exploration Geophysics, Houston, Texas, 1959. *A comprehensive presentation of the fundamentals of seismic computation and interpretation as given in a series of lessons by the author. Published as a Memorial Volume to him.*

Economic Mineral Deposits, 2nd Edit. ALAN M. BATEMAN. Pp. 916. *Modern Asia Edition.* Charles E. Tuttle Co., Tokyo, Japan. Price, yen 1,480. *A reprinting in English at Tokyo for Asian distribution.*

Organic Chemistry—A Brief Course, 2nd Edit. R. Q. BREWSTER and W. E. MCEWEN. Pp. 401; figs. 25. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1959. Price, $10.00 and $7.50. *A systematic treatment of families of carbon compounds; classes of hydrocarbons and their derivatives; sulfur and nitrogen; acid derivatives; dyes; processes and products. Comprehensive, yet brief.*

Saudi Arabia: Its People, Its Society, Its Culture. G. A. LIPSKY and others. Pp. 367; maps 4. Human Relations Area Files Press, Taplinger Publ. Co., New York, 1959. Price, $7.00. *The impact of oil and ensuing wealth affecting Saudi society and Arab relationships with the West.*

Permian Productacea of Western Australia. P. J. COLEMAN. Pp. 148; pls. 21; figs. 6; tbls. 3. Bureau of Mineral Resources, Geology and Geophysics, Commonwealth of Australia, Bull. 40, 1957. *Description and discussion of 34 species belonging to the brachiopod super-family Productacea.*

Paléolithique ancien à Léopoldville. HENDRIK VAN MOORSEL. Pp. 23; figs. 3; pls. 10. Les Editions de l'Universite Lovanium de Leopoldville, Belgian Congo, 1959. *Brief geologic and archeological report on the surficial deposits and associated artifacts of the Leopoldville Plain.*

Conge Belge, Topographic Maps, Scale 1: 200,000. Feuilles, Haut-Lomami, and Sokele.

Congo Belge et Ruanda, Carte Geologique, Scale 1: 50,000. Sheets VAK S6/15NW4, SW4, SW3, SW1, SW2; 6/14 SW2; SW4.

British Territories in Borneo Annual Report of the Geological Survey Department for 1958. F. W. Roe. Pp. 247; pls. 50; figs. 44; tbls. 32. Price, 7s. Kuching, Sarawak, 1959. *The exporting of bauxite from Sarawak began in 1958. Progress of geologic mapping and researches is reported in short papers by several authors.*

Stratigraphy and Structure of the Salmo Lead-Zinc Area. J. T. Fyles and C. G. Hewlett. Pp. 162; pls. 16; figs. 20; tbls. 4. British Columbia Department of Mines Bull. 41. 1959. *Excellent, well illustrated geologic report concerning lead-zinc replacement deposits in highly folded and faulted Cambrian sediments.*

Outline of the Geology of the Ruwenzori Mountains. R. B. McConnell. Pp. 245–266; pls. 7. British Guiana Geological Survey, 1959. *Preliminary account of stratigraphy and structure of the Ruwenzori Mountains from the 1951–1952 expedition. Reprinted from Overseas Geology and Mineral Resources Vol. 7, No. 3.*

Geological Reconnaissance of Parts of the Central Islands of the British Solomon Islands Protectorate. Univ. of Sydney Dept. of Geology and Geophysics. Pp. 267–306; pls. 8; figs. 3; colored maps 3. Geological Survey of the British Solomon Islands Protectorate, Special Paper 1. 1957. *Deposits of manganese, gold, chromite, asbestos, and petroleum were noted. Reprinted from Colonial Geology and Mineral Resources Vol. 6, No. 3.*

Geology of the Country around Polonnaruwa. W. Vitanage. Pp. 75; pls. 12; figs. 11; tbls. 12. Geological Survey of Ceylon, Memoir 1, 1959. *A well-illustrated report concerning chiefly the petrology and structural geology of a Precambrian terrain.*

Proceedings of the Geological Society of China, Number 2 for 1959. Pp. 173; pls. 15; figs. 46; tbls. 41. Published by the Society, Taipei, Taiwan, China, 1959. *The six main articles concern various studies in areas of Taiwan—gabbroic rocks; structural patterns; biostratigraphic study of the Miocene; hydrothermal alteration of dacite, clay deposits; and sulfur-melnikovite deposits. In English.*

Third Symposium on Rock Mechanics. Pp. 366; figs. 168; tbls. 34. Price, $3.00. Quarterly of the Colorado School of Mines, Vol. 54, No. 3, Golden, 1959. *This third symposium featured 20 papers plus discussions divided into 4 major groups: 1) Factors Common to Comminution, Underground Failures, and Failures Resulting from Explosions; 2) Factors Common to Soil Mechanics and Rock Failure; 3) Explosions and Seismology; 4) Nuclear Blasts in Mining.*

Über Radioaktive und Uranhaltige Thermalsedimente, Insbesondere von Baden-Baden. Franz Kirchheimer. Pp. 67; pls. 7; figs. 9. Geologischen Landesamtes in Baden-Württemberg, Heft 3, Freiburg, 1959. *Five papers concerning the radioactivity and uranium-bearing sediments associated with the thermal springs of Baden-Baden.*

Report of the Director of Geological Survey for the Period 1st April, 1957, to 31st March, 1958. Pp. 16; tbls. 1. Price 1 shilling and sixpence. Ghana, 1959. *Summary of work and activities of the Survey for 1957.*

Geology of Buda Quadrangle, Illinois. PAUL MACCLINTOCK and H. B. WILLMAN. Pp. 29; pl. 1; figs. 4; tbls. 7. Illinois State Geological Survey Circ. 275, Urbana, 1959. *Description of complex glacial deposits in northwestern Illinois.*

Oil and Gas Developments in Kansas During 1958. E. D. GOEBEL, P. L. HILPMAN, and D. L. BEENE. Pp. 228; pls. 3; figs. 11; tbls. 33. Kansas Geological Survey, Bull. 138, Lawrence, 1959. *Oil production in Kansas during 1958 decreased 3.3% from the previous year.*

Official Oil in North Dakota First Half 1959. Pp. 88. North Dakota Geological Survey, Grand Forks, 1959. Price, $2.00.

Mineral Map of Northern Rhodesia, scale 1: 2,000,000. *Brief summary of mine production.*

Geologic Map of Nouvelle Caledonie, Hienghene-Voh, scale 1: 100,000.

Preliminary Report on a Regional Stratigraphic Study of Devonian Rocks of Pennsylvania. T. H. JONES and A. S. CATE. Pp. 5; pls. 7; fig. 1. Pennsylvania Geological Survey Fourth Series Spec. Bull. 8, Harrisburg, 1957. *Summary of available information and literature on the Devonian of Pennsylvania, from which, a series of regional isopach and lithofacies maps were compiled.*

Petrogenetic Significance of Gneiss Blocks Partly Melted by Hyperite Magma. PONTUS LJUNGGREN. Pp. 75–90; figs. 3. Institutes of Mineralogy, Paleontology, and Quaternary Geology, Univ. of Lund, Sweden, Publ. 65. Reprinted from Kungl. Fysiografiska Sällskapets i Lund Förhandlingar Bd. 29, Nr. i. *While biotite and hornblende do not seem to be affected by recrystallization of these blocks, microcline changed to orthoclase and large phenocrysts were formed. In English.*

On Zoned Granitis Pegmatites. O. BROTZEN. Pp. 71–81. Price, 2.50 Sw. kr. Univ. of Stockholm Contributions in Geology, Vol. III:3. *Magmatic and metamorphic origins for pegmatite magmas are considered. Mineral distribution is discussed. In English.*

Mineral Industries and Resources of Virginia. Map, scale 1: 500,000. Compiled by E. O. GOOCH and R. F. PHARR. *Gives general geology and location of major mineral deposits. Brief summary of statistics for the mineral industry.*

Collie Mineral Field. G. H. LOW. Pp. 134; pls. 5; figs. 3; tbls. 14. Maps, scale 30 chains to an inch.

Western Australia Geological Survey Bull. 105—Pt. 2. Perth, 1958. *Results of an extensive drilling program indicate reserves of 1,877 million tons of extractable coal.*

Tectonic Sketch Map of North America. W. T. THOM, JR. Scale 1: 10,000,000. *Map shows general regional structural features and approximate configuration of the surface of the basement complex. Includes a detailed inset of tectonic provinces adjacent to the Williston Basin.*

University of Arizona Press—Tucson, 1959.

Univ. of Arizona Bull. Vol. XXX, No. 1. Petrology. G. M. BUTLER. Pp. 29; figs. 2; tbls. 2. Price, 50 cents. *A simplified introduction to petrology for the layman.*

Univ. of Arizona Bull. Vol. XXX, No. 2. Minerals of Arizona. F. W. GALBRAITH and D. J. BRENNAN. Pp. 1–116. Price, $1.00. *A complete listing of all minerals, including distinctive characteristics and occurrences, found in the state.*

University of California Press—Berkeley, 1959.

Tertiary Stratigraphy of the Blairsden Quadrangle Plumas County, California. CORDELL DURRELL. Pp. 161–192; pls. 24–29; fig. 1; Maps, 5. Price, $1.00. Univ. California Publications in Geological Sciences, Vol. 34, No. 3. *Description of eight formations, dominantly of volcanic origin, ranging in age from Middle Eocene to Plio-Pliestocene.*

The Lovejoy Formation of Northern California. CORDELL DURRELL. Pp. 193–220; pl. 1; maps 4. Price, $1.00. Univ. California Publications in Geological Sciences Vol. 34, No. 4. *A study of the tertiary basaltic lavas of this area indicates they are part of a once continuous sheet called the Lovejoy Formation.*

California Division of Mines—San Francisco, 1959.

Spec. Rept. 55. Franciscan Chert in California Concrete Aggregates. H. B. GOLDMAN. Pp. 28; pls. 17; figs. 8; tbls. 5. Price, 50 cents. *Providing the alkali content of the cement is controlled, Franciscan chert can be used in any proportion as the aggregate for serviceable concrete.*

Spec. Rept. 56. Limestone and Dolomite in the Northern Gabilan Range, California. O. E. BOWEN, JR. and C. H. GRAY, JR. Pp. 40; pls. 36; figs. 4. Price, 50 cents. *Description of limestone and dolomite deposits, occurring as pendants suspended in crystalline basement rocks, utilized as industrial raw materials.*

Bureau d'Etudes Geologiques et Minières—Paris, 1959.

La Chronique des Mines d'Outre-Mer et de la Recherche Minière (Mensuelle), Numéro Spécial. Symposium sur la Geologie de l'Uranium en Afrique. Pp. 280–331. Price, 350 franc per issue. *Discussion of prospecting techniques employed and various uranium occurrences in Africa.*

Supplement a la Chronique des Mines d'Outre-Mer and de la Recherche Minière, No. 277. Pp. 25. *Journal lists translations, abstracts, and other functions performed by this Service.*

Direction des Mines et de la Geologie de l'Afrique Equatoriale Francaise, Brazzaville, 1958.

Notice Explicative sur la Feuille Bangui-Est. F. FOGLIERINE and J.-L. MESTRAUD. Pp. 30. Maps, scale 1/500.000. *Brief petrographic report concerning rocks of a metamorphic terrain.*

Notice Explicative sur la Feuille Ouesso. J. SONET. Pp. 22; tbl. 1. Maps, scale 1/500.000. *Geology of a dominantly metamorphic terrain in French Equatorial Africa. Several placer deposits of ilmenite were derived from the weathering of dolerites.*

Notice Explicative de la Carte Geologique Provisoire du Borkou-Ennedi-Tibesti au 1/1.000.000. PH. WACRENIER. Pp. 24; maps 2. *Brief report accompanying the geologic map of Borkou-Ennedi-Tibesti.*

Consiglio Nationale Delle Ricerche—Rome, 1958–59.

Publicazione N. 142. Sul significato della presenza di metano nelle manifestazioni esalative e idrotermali. A. DI NOI. Pp. 241–247; figs. 3; tbls. 2. (Reprinted from "Annali di Geofisica," Vol. XI, n. 3–4, 1958.) *A physicochemical study of the problem suggests that the presence of methane in exhalative and hydrothermal solutions is compatible with a juvenile origin of such fluids.*

Publicazione N. 153. Centro di studio per la geologia tecnica attività svolta dal 1° novembre 1957 al 31 ottobre 1958. Pp. 34; tbls. (Reprinted from "La Ricerca Scientifica," Anna 29°, N. 4, Aprile, 1959.) *Intrinsical and extrinsical characteristics of rocks and soils as applied to hydrology and geomorphology.*

Publicazione N. 154. Notizie preliminari sui lavori di rilevamento di dettaglio delle caratteristiche del giacimento lignitifero del Mercure (Province di Potenza e Cosenza). FILIPPO FALINI. Pp. 23; figs. 8.

Geological Survey of Japen—Hisamoto-chō, Kawasaki-shi, 1959.

Explanatory Text of the Geological Map of Japan. Toinomisaki (Kagoshima-97). YOSHITO KINO. Pp. 22; pls. 8; fig. 1; tbls. 4. Map, scale 1:50,000. *Description of late Cenozoic sediments with minor associated volcanics and intrusives. In Japanese; English summary.*

Explanatory Text of the Geological Map of Japan. Obi (Kagoshima-91). YOSHITO KINO. Pp. 31; pls. 25; fig. 1; tbls. 2; pls. 24. Map, scale 1:50,000. *Description of late Cenozoic sediments and natural gas occurrences of this district. In Japanese; English summary.*

Explanatory Text of the Geological Map of Japan. Kanazawa (Kanazawa-26). ISAO IMAI. Pp. 30; figs. 10; tbls. 4. Map, scale 1:50,000. *Limited production of natural gas is obtained from Quaternary sediments. In Japanese; English summary.*

Southern Rhodesia Geological Survey—Salisbury, 1959.

Short Rept. 36. Explanation of the Geological Map of the Country Around Salisbury. R. TYNDALE-BISCOE. Pp. 1–10. *Brief description of geology around Salisbury.*

Short Rept. 37. The Geology of a Portion of the Inyanga District. R. TYNDALE-BISCOE. Pp. 1–11. Geol. Map, scale 1:250,000. *Brief geologic description of a dominantly metamorphic terrain.*

Bull. 46. The Geology of the Country around Mangula Mine, Lomagundi and Urungwe Districts. J. G. STAGMAN. Pp. 84; pls. 6; tbls. 4. Map, scale 1:100,000. *Geology of an area composed dominantly of rocks of the Momagundi System and the Piriwire Series, in which Southern Rhodesia's largest copper producer is located.*

Stockholms Högskolas Mineralogiska Institut—Stockholm, 1959.

N:o 223. Outline of Mineralization in Zoned Granitic Pegmatites. A Qualitative and Comparative Study. O. BROTZEN. Pp. 98; figs. 30. In English. (Reprinted from Geologiska Föreningens I Stockholm Förhandlingar, Jan.–Feb., 1959.) *The author believes internal zoning developed rapidly and not in response to secular changes in geologic conditions. He rejects the concept of harmony between mineral association in pegmatites and degree of metamorphism in the surrounding region.*

N:o 224. Mineral-Association in Granitic Pegmatites. A Statistical Study. O. BROTZEN. Pp. 231–296; figs. 7; tbls. 21. In English. (Reprinted from Geologiska Föreningens I Stockholm Förhandlingar, March–April, 1959.) *A study of the association between typical accessory minerals found in granitic pegmatites and the major constituents.*

Bureau of Economic Geology, The University of Texas—Austin, 1959.

Geol. Quadrangle Map 23. Geology of Van Horn Mountains, Texas. P. C. TWISS. Map, scale 1:48,000. *Brief description of general geology on map margin.*

Rept. of Investigations 39. Correlation of the Ogallala Formation (Neogene) in Western Texas With Type Localities in Nebraska. J. C. FRYE and A. B. LEONARD. Pp. 46; pls. 2; figs. 3. *Correlation based on three floral zones from the Ogallala of West Texas.*

Rept. of Investigations 40. Vermiculite in Central Texas. S. E. CLABAUGH and V. E. BARNES. Pp. 32; figs. 6; tbls. 2. *Vermiculite deposits, formed by the weathering of biotite, occur in Precambrian metamorphic rocks of Central Texas.*

Union of South Africa Geological Survey—Pretoria, 1957.

Explanation of Geologic Map Sheet 62. Vereeniging. L. T. NEL and H. JANSEN. Pp. 90; figs. 2. Price, 5s. Map, scale 1:125,000.

Sheet 42. Soutpansberg. Scale, 1:125,000.

Geologic and gravity maps in 4 sheets. Scale, 1:500,000.

Geologic map 2228. Biet Bridge. Scale, 1:250,000.

Geologic map 2230. Messina. Scale, 1:250,000.

West Virginia Geological Survey—Morgantown, 1958–59.

The Mineral Industry of West Virginia (1956–57). J. R. KERR and JEAN PENDLETON. Pp. 17; tbls. 7. *Colored geologic map, scale 1:500,000, with location of mineral deposits. Mineral production increased 5 percent in value during 1957 over the previous year.*

Mineral Resources and Mineral Industries. P. H. PRICE. Map, scale 1:500,000.

U. S. Geological Survey—Washington, D. C., 1959.

Bull. 1039-C. Haydite Raw Material in the Kings River, Sutton, and Lawing Areas, Alaska. R. A. ECKHART and GEORGE PLAFKER. Pp. 33–65; pls. 4; figs. 4; tbls. 6. *Favorable laboratory tests and large reserves of this argillaceous material from the area indicate it to be a good raw material source for haydite.*

Bull. 1046-R. Uranium in Sharon Springs Member of Pierre Shale South Dakota and Northeastern Nebraska. R. C. KEPFERLE. Pp. 577–604; pls. 4; figs. 8; tbls. 6. *Minor uranium mineralization is believed to have taken place during or shortly after deposition of this black organic marine shale.*

Bull. 1052-I. Equation of Continuity in Geology with Applications to the Transport of Radioactive Gas. A. Y. SAKAKURA, CAROLYN LINDBERG, and HENRY FAUL. Pp. 287–305; figs. 6; tbls. 2. Price, 15¢. *Discussion of experimental and theoretical aspects of radon gas flow and applied to selected data from the Texas Panhandle gas field.*

Bull. 1052-J. Electrical Properties of Sandstones of the Morrison Formation. G. V. KELLER. Pp. 307–344; pls. 2; figs. 14; tbls. 3. *Resistivity of sandstone members of the Morrison formation is higher in those portions most favorable for the occurrence of ore.*

Bull. 1060-D. Geology and Construction-Material Resources of Nemaha County, Kansas. M. R. MUDGE, C. P. WALTERS, and R. E. SKOOG. Pp. 179–256; pls. 2; figs. 2; tbl. 1. *Outwash gravels and glaciolacustrine deposits comprise the economic sources of construction materials at present.*

Bull. 1068. Geology of Wabaunsee County Kansas. M. R. MUDGE and R. H. BURTON. Pp. 210; pls. 19; tbls. 2; figs. 3. *Sediments of Pennsylvanian, Permian, and Quaternary age crop out in Wabaunsee County. Some are utilized in certain phases of construction engineering.*

Bull. 1072-C. Coal Resources of Colorado. E. R. LANDIS. Pp. 131–232; pls. 2; figs. 2; tbls. 16. *For areas where information is adequate, approximately 40.4 billion tons of recoverable coal is estimated to underlie Colorado.*

Bull. 1074-C. Stratigraphy of the Area Between Hernando and Hardee Counties, Florida. K. B. KETNER and L. J. MCGREEVY. Pp. 49–124; pls. 3; figs. 3; tbls. 2. Pp 49–124; pls. 3; figs. 3; tbls. 2. *Rocks previously interpreted as the Pliocene Alachua and Bone Valley formations are reassigned to the lower and middle Miocene Tampa and Hawthorn formations.*

Bull. 1074-D. Geology of Uranium Deposits in Triassic Rocks of the Colorado Plateau Region. W. I. FINCH. Pp. 125–164; pls. 5; figs. 2. *The Uranium deposits in Triassic rocks of the Plateau is attributed to redeposition of uranium and associated metals in favorable sedimentary and tectonic structures by ground waters which leaked from them overlying sediments.*

Bull. 1075. Bibliography of North American Geology, 1956. RUTH R. KING and others. Pp. 554. Price, $1.75. *Author and subject indexes.*

Bull. 1083-A. Periodic Heat Flow in a Stratified Medium with Application to Permafrost Problems. A. H. LACHENBRUCH. Pp. 1–36; pls. 3; figs. 8; tbls. 3. *A theoretical approach to the thermal properties of stratified earth materials indicates its useful application to gravel-fill and other problems.*

Bull. 1083-B. Directional Resistivity Measurements in Exploration for Uranium Deposits on the Colorado Plateau. G. V. KELLER. Pp. 37–72; figs. 20; tbls. 5. *Directional-resistivity methods may enable the investigator to predict favorable locations for the occurrence of uranium at distances of 600–1000 feet.*

Bull. 1083-C. Dissipation of the Temperature Effect of Drilling a Well in Arctic Alaska. A. H. LACHENBRUCH and M. C. BREWER. Pp. 73–109; figs. 7; tbls. 8. *A six-year study of the upper 600 feet of a 2900 foot well indicates that about 50 years will elapse before the temperature disturbance caused by drilling diminishes to 0.01° C.*

Bull. 1084-C. Selenium Content of Some Volcanic Rocks from Western United States and Hawaiian Islands. D. F. DAVIDSON and H. A. POWERS. Pp. 69–81; figs. 3; tbls. 4. *It is suggested that crystalline volcanic rocks have lost, during crystallization, the selenium contained in the parent magma.*

Bull. 1084-D. Geochemistry of Uranium in Phosphorites and Black Shales of the Phosphoria Formation. R. P. SHELDON. Pp. 83–113; figs. 7; tbls. 6. *There is a higher concentration of uranium in those phosphatic sediments that were deposited in an environment of low Eh than in those phosphatic sediments that were deposited in an environment of high Eh.*

Bull. 1084-E. Distribution of Chemical Elements in the Salt Wash Member of the Morrison Formation, Jo Dandy Area Montrose County, Colorado. W. L. NEWMAN and D. P. ELSTON. Pp. 117–150; figs. 3; tbls. 3. *There appears to be no significant relation between the chemical composition of sandstone or mudstone and distance from known mineralized areas.*

Bull. 1087-B. Uranium Resources of the Cedar Mountain Area Emery County, Utah, A Regional Synthesis. H. S. JOHNSON, JR. Pp. 23–57; figs. 6; tbl. 1. Price, 20 cents. *Field reconaissance and other studies suggest that further discovery of sandstone-type uranium deposits will be made in the area if primary sedimentary features are the dominant ore control.*

Bull. 1106-B. Geophysical Abstracts 177, April–June, 1959. DOROTHY B. VITALIANO, S. T. VESSELOWSKY, and others. *Abstracts of current literature pertaining to the physics of the solid earth and to geophysical exploration.*

Prof. Paper 294-L. Brachiopod Fauna of Saturday Mountain Formation, Southern Lemhi Range, Idaho. R. J. Ross, Jr. Pp. 441–461; pls. 3; figs. 10; tbls. 2. *Poor sorting by size or shape of shells suggests that these silicified brachiopods accumulated under quiet bottom conditions.*

Prof. Paper 306-B. Geology and Paleontology of Canal Zone and Adjoining Parts of Panama. Description of Tertiary Mollusks (Gastropods: Vetmetidae to Thaididae). W. P. Woodring. Pp. 147–239; pls. 15; tbls. 15.

Prof. Paper 314-H. Pre-Atoka Rocks of Northern Arkansas. S. E. Frezon and E. N. Glick. Pp. 171–189; pls. 12; fig. 1; tbl. 1. *Five zones have produced commercial quantities of gas. Oil may be present in small pools.*

Prof. Paper 315-A. Geology of Part of the Horseshoe Atoll in Scurry and Kent Counties, Texas. P. T. Stafford. Pp. 20; pls. 9; figs. 5; tbls. 4. *The cyclic growth of this reef-like structure is believed to be related to changes in sea level within the Midland Basin during late Pennsylvanian and early Permian time.*

Prof. Paper 315-B. Geology of Part of the Horseshoe Atoll in Borden and Howard Counties, Texas. R. J. Burnside. Pp. 21–35; pls. 5; figs. 3; tbls. 3. *Numerous oil accumulations probably occurred during Wolfcamp time shortly after the atoll was covered by black shale.*

Prof. Paper 317-C. Geology of Isla Mona Puerta Rico, and Notes on Age of Mona Passage. C. A. Kaye. Pp. 141–178; pls. 3; figs. 6; tbls. 6. Price, 65 cents. *Rocks of this small island of the Greater Antilles are almost exclusively Cenozoic carbonates.*

Prof. Paper 318. Occurrence of Nonpegmatite Beryllium in the United States. L. A. Warner, W. T. Holser, V. R. Wilmarth and E. N. Cameron. Pp. 198; pls. 5; figs. 60; tbls. 82. Price, $2.25. *Extensive survey of nonpegmatite occurrences of beryllium in the United States indicates that at present no commercial deposits are available.*

Water-Supply Paper 1320-E. Summary of Floods in the United States During 1953. J. V. B. Wells. Pp. 341–364; figs. 2; tbl. 1. Price, 20 cents.

Water-Supply Paper 1370-C. Summary of Floods in the United States During 1954. J. V. B. Wells. Pp. 201–263; pls. 4; figs. 29; tbls. 23. *The heaviest floods occurred in Iowa, Texas, Colorado, New Mexico, the Chicago area, and the Eastern States.*

Water-Supply Paper 1375. Ground-Water Resources of Riverton Irrigation Project Area, Wyoming. D. A. Morris, O. M. Hackett, K. E. Vanlier, and E. A. Moulder. **Section on Chemical Quality of Ground Water.** W. H. Durum. Pp. 205; pls. 6; figs. 28; tbls. 18. *The Wind River formation (Eocene) furnishes most of the water for domestic use, but is considered an insufficient source for irrigation.*

Water-Supply Paper 1422. Geology and Ground-Water Resources of Medina County, Texas. C. I. R. Holt, Jr. Pp. 213; pls. 6; figs. 14; tbls. 12. *Movement of water in the Edwards limestone of Cretaceous age, the principal aquifer, is generally southeastward, but it is locally controlled by faults.*

Water-Supply Paper 1461. Geology, Hydrology, and Chemical Character of Ground Waters in the Torrance-Santa Monica Area, California. J. F. Poland, A. A. Garretti, and Allen Sinnott. Pp. 425; pls. 20; figs. 34; tbls. 31. Two maps in pocket, scale 1:31,680. *Expanding population and industry in this area have drawn down local ground water levels as much as 70 feet below sea level and have resulted in local saline contamination. Local recharge is the only feasible means of correcting this situation.*

Water-Supply Paper 1469. Ground-Water Conditions and Storage Capacity in the San Joaquin Valley, California. G. H. DAVIS, J. H. GREEN, F. H. OLMSTED, and D. W. BROWN. Pp. 287; pls. 29; figs. 8; tbls. 10. *Adequate ground-water resources of the San Joaquin Valley are subdivided both horizontally and vertically according to differences in quality.*

Water-Supply Paper 1471. Hydrology of the Long Beach-Santa Ana Area, California. Pp. 257; pls. 11; figs. 9; tbls. 29. Map in pocket, scale 1:31,680. *Three methods are suggested to prevent the further encroachment of saline waters from the coast into the present reservoirs of this highly industrializd area.*

Water-Supply Paper 1478. Ground-Water Resources of the Middle Big Wood River-Silver Creek Area, Blaine County, Idaho. R. O. SMITH. Pp. 64; pls. 5; figs. 9. *Controlled withdrawal of ground-water reserves should supply the additional water needed for irrigation in this area.*

Economic Geology
Vol. 54, 1959, pp. 1593–1594

SCIENTIFIC NOTES AND NEWS

HOLLIS D. HEDBERG, President-elect of the Geological Society of America and formerly Vice-president of The Gulf Oil Company has been appointed professor in the Department of Geology, Princeton University.

PAUL BARTHOLOMÉ, professor at the University of Louvanium, Leopoldville, Belgian Congo, is giving a series of lectures in crystal physics at Princeton University.

JOHN WILKINSON, Professor of Geology at the University of New England, Armidale, New South Wales, Australia, is serving this year as a Fulbright exchange professor at Princeton University, giving instruction in petrology at both the undergraduate and graduate levels.

ROGER DE WIEST has been appointed an assistant professor in Geological Engineering at Princeton University to develop research and instruction in underground fluids, particularly ground water.

JAMES GILLULY has been appointed Staff Scientist of the U. S. Geological Survey. THOMAS A. HENDRICKS succeeds him as Chief of the Fuels Branch.

EDWARD R. BORCHERDT and C. DEWITT SMITH announce their association as mining consultants at 369 Pine Street, San Francisco 4, California.

FRANCIS R. HALL, formerly with the U. S. Geological Survey in Louisville, Kentucky, has joined the staff of Stanford Research Institute as a geologist to expand water research effort in SRI's Physical Sciences Division.

ELLIS B. HERRINGTON, JR. formerly geologist for American Smelting and Refining Co., has accepted the position of assistant geologist of the Silver City, N. Mexico, operations of the Kennecott Copper Corp.

ROBERT I. DAVIS has accepted the position of Assistant Professor of Geology at St. Louis University in Webster Groves, Mo. He was for five years prior to this a geologist for Cia. Minera de Penoles, S. A.

FRED H. HOWELL, senior geologist with Kennecott Copper Co. has transferred from the Braden Copper Co. in Rancagua, Chile, to Salt Lake City and is making his home at 2610 East Milo Way.

ROBERT H. STEBBINS has joined the staff of Hunting Technical Services Inc. in New York, as chief geologist. He was formerly geologist with the Raw Materials Exploration Div., Columbia Iron Mining Co., U. S. Steel Corp.

CHARLES A. ANDERSON has been appointed to succeed Dr. Wilmot H. Bradley as Chief Geologist of the U. S. Geological Survey.

The Ninth National Clay Conference will be held at Purdue University, Lafayette, Indiana, on October 6, 7, and 8, 1960, under the auspices of the City Minerals Committee of the National Academy of Sciences—National Research Council. The symposia of invited papers will be held on the topics of "Engineering Aspects

of Physico-Chemical Properties of Clays" and "Clay-Organic Complexes." In addition to these special symposia there will be general sessions of contributed papers. All those having contributions should contact Dr. J. L. White, Chairman, Ninth National Clay Conference, Agronomy Department, Purdue University, Lafayette, Indiana. The title and an abstract of approximately 250 should be sent in by June 1.

ERNEST K. LEHMANN, partner in the firm of Lindgren & Lehmann, Consulting Mining Geologists, Minneapolis and St. Paul, Minnesota, has left the United States for a consulting assignment in Argentina.

DR. THOMAS B. NOLAN, Director of the U. S. Geological Survey, presided over the dedication of its new topographic mapping facilities at its Menlo Park Center, California, on November 24. The new facilities are designed to produce r9 new or revised topographic maps each month. It takes about three years to complete each one, and approximately 1,500 Pacific area map manuscripts are in process at all times.

The University of Minnesota announces the following recent appointments in the Department of Geology: DR. TIBOR ZOLTAI, Assistant Professor in mineralogy and crystallography, and DR. WILLIAM C. PHINNEY, Assistant Professor in petrography and petrology. (A correction.)

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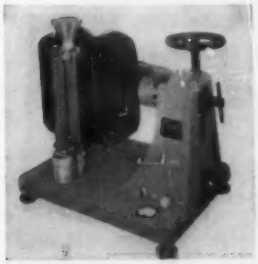

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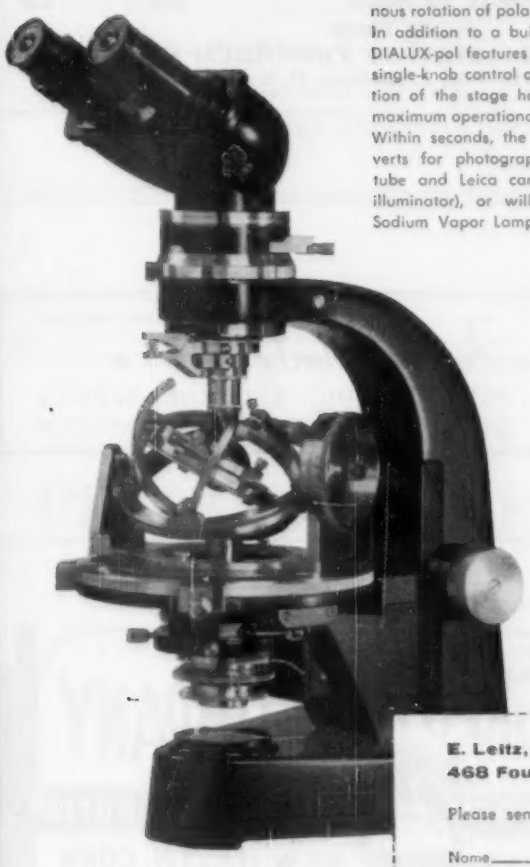

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